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(54) **Iron oxide hydroxide composite particles, pigment, paint and resin composition.**

(57) Iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , comprises:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of said iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic pigment coat formed on said coating layer comprising said organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of said iron oxide hydroxide particles.

The iron oxide hydroxide composite particles of the present invention contain no harmful elements and exhibit not only excellent chemical resistances such as acid resistance and alkali resistance, but also excellent heat resistance.

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## Description

**[0001]** The present invention relates to iron oxide hydroxide composite particles, a pigment composed of the same, a paint containing the pigment, a resin composition containing the pigment and a process for producing the iron oxide hydroxide composite particles. More particularly, the present invention relates to iron oxide hydroxide composite particles containing no harmful elements and exhibiting not only excellent chemical resistances such as acid resistance and alkali resistance, but also excellent heat resistance, a pigment such as a green-based pigment or an orange-based pigment, composed of the iron oxide hydroxide composite particles, a paint containing the pigment, a resin composition containing the pigment and a process for producing the iron oxide hydroxide composite particles.

**[0002]** At present, as green-based pigments, there have been widely used inorganic pigments such as chrome green, chromium oxide and zinc green, and organic pigments such as phthalocyanine green. Also, as orange-based pigments, there have been used chrome vermilion, chrome orange, permanent orange, benzidine orange or the like. These pigments have been extensively applied to colorants of resins, paints, printing inks or the like.

**[0003]** However, it is known that the inorganic pigments such as chrome green, chromium oxide and zinc green tend to be deteriorated in chemical resistances such as acid resistance and alkali resistance though they are excellent in light resistance, and are expensive.

**[0004]** In addition, the inorganic pigments such as chrome green, chromium oxide and zinc green contain harmful elements such as lead and chromium. For this reason, it has been strongly required to develop alternate materials for these green-based pigments from viewpoints of hygiene, safety and environmental protection.

**[0005]** On the other hand, the organic green-based pigments such as phthalocyanine green exhibit a high tinting strength and a clear hue. However, it is known that these organic pigments are deteriorated in light resistance, i.e., suffer from bronze-bleeding (so-called bronzing) upon outdoor exposure.

**[0006]** Chrome vermilion and chrome orange exhibit a very clear hue. However, it is known that these orange-based pigments are deteriorated in chemical resistances such as acid resistance and alkali resistance as well as light resistance and heat resistance, and are extensive.

**[0007]** In addition, the inorganic orange-based pigments such as chrome vermilion and chrome orange also contain harmful elements such as lead and chromium. Therefore, it has been strongly required to develop alternate materials for these orange-based pigments from viewpoints of hygiene, safety and environmental protection.

**[0008]** It is also known that the organic orange-based pigments such as permanent orange and benzidine orange exhibit a clear hue, but are deteriorated in light resistance.

**[0009]** Further, resin compositions using thermoplastic resins such as polyolefins, for example, polyethylenes, polypropylenes, styrene polymers or the like, polyamides and ABS resins are usually molded at a temperature as high as not less than 200°C. For this reason, pigments added as colorants to these resin compositions are required to exhibit a good heat resistance.

**[0010]** In consequence, green and orange-based pigments added to these resin compositions are strongly required to have not only excellent chemical resistances and tinting strength but also excellent heat resistance.

**[0011]** Hitherto, in order to improve properties of the pigments, it has been attempted to use inorganic and organic pigments in combination. For example, there have been proposed methods of co-precipitating chrome yellow and phthalocyanine blue together or adhering organic pigments onto the surfaces of inorganic pigments (Japanese Patent Application Laid-Open (KOKAI) Nos. 4-132770(1992), 10-88032(1998) and 11-181329(1999), etc.).

**[0012]** Thus, it has been strongly demanded to provide green and orange-based pigments exhibiting both excellent chemical resistances and excellent heat resistance without containing harmful elements. However, such pigments capable of satisfying these requirements have not been provided until now.

**[0013]** Namely, in the above method of co-precipitating chrome yellow and phthalocyanine blue together, the obtained pigments show a toxicity due to chrome yellow. Further, paints containing such pigments are insufficient in storage stability due to the use of co-precipitated pigments, so that coating films formed therefrom tend to suffer from bleeding.

**[0014]** In the method of precipitating organic pigments in the presence of inorganic pigments as described in Japanese Patent Application Laid-Open (KOKAI) No. 4-132770, the organic pigments are insufficient in adhesion to the inorganic pigments.

**[0015]** In the method of mechanically mixing and milling inorganic and organic pigments together as described in Japanese Patent Application Laid-Open (KOKAI) No. 10-88032(1998), the organic pigments are also insufficient in adhesion to the inorganic pigments.

**[0016]** Further, in Japanese Patent Application Laid-Open (KOKAI) No. 11-181329(1999), there is described the method of adding organic pigments to a solution prepared by dissolving organopolysiloxane in cyclic silicone to disperse therein the pigments as fine particles, impregnating the fine organic pigments with high oil-absorption inorganic pigments, and then evaporating cyclic silicone from the pigments. In this method, the organic pigments are also insufficient in adhesion to the inorganic pigments.

**[0017]** Meanwhile, in Japanese Patent Application Laid-Open (KOKAI) No. 11-323174(1999), there are described

iron-based black composite particles obtained by forming an organosilane coating layer on black iron oxide particles or black iron oxide hydroxide particles, and then forming a carbon black coat on the organosilane coating layer. Since the iron-based black composite particles are black iron oxide hydroxide composite particles having the carbon black coat, the iron-based black composite particles are quite different from composite particles having green or orange-based pigments.

**[0018]** As a result of the present inventors' earnest studies, it has been found that by mixing as core particles iron oxide hydroxide particles with at least one compound selected from the group consisting of:

- (1) alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes,

by using an apparatus capable of applying a shear force to the core particles, thereby coating the surface of the black iron oxide hydroxide particle with the compounds;

mixing the obtained iron oxide hydroxide particles coated with the compounds and organic blue or red-based pigment in an amount of 1 to 30 parts by weight based on 100 parts by weight of the core particles by using an apparatus capable of applying a shear force to the core particles, thereby forming organic blue or red-based pigment coat on the surface of a coating layer comprising the organosilicon compounds, the thus obtained iron oxide hydroxide composite particles are harmless pigments which are excellent not only in chemical resistances such as acid resistance and alkali resistance, but also in heat resistance. The present invention has been attained on the basis of the above finding.

**[0019]** An object of the present invention is to provide a harmless pigment such as a harmless green or orange-based pigment exhibiting not only excellent chemical resistances such as acid resistance and alkali resistance, but also high hiding power, high tinting powder and excellent heat resistance.

**[0020]** Another object of the present invention is to provide a fine pigment such as a green or orange-based fine pigment which contains no harmful elements and is improved not only in chemical resistances such as acid resistance and alkali resistance but also in heat resistance, and further is capable of producing a paint and a resin composition exhibiting an excellent transparency.

**[0021]** To accomplish the aim of the present invention, in a first aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter (average major axial diameter) of 0.005 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0022]** In a second aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coat formed on at least a part of the surface of the iron oxide hydroxide particles, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon;  
a coating formed on surface of the said coat, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0023]** In a third aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter of from 0.005 to less than 0.1  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic blue-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 5 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0024]** In a fourth aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter of from 0.005 to less than 0.1  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coat formed on at least a part of the surface of the iron oxide hydroxide particles, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon;  
a coating formed on surface of the said coat, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic blue-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 5 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0025]** In a fifth aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter of from 0.005 to less than 0.1  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic red-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0026]** In a sixth aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter of from 0.005 to less than 0.1  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coat formed on at least a part of the surface of the iron oxide hydroxide particles, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon;  
a coating formed on surface of the said coat, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic red-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0027]** In a seventh aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter of from 0.1 to 1.0  $\mu\text{m}$ , comprising:



iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic blue-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 5 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0028]** In an eighth aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter of from 0.1 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coat formed on at least a part of the surface of the iron oxide hydroxide particles, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon;  
a coating formed on surface of the said coat, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic blue-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 5 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0029]** In a ninth aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter of from 0.1 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic red-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0030]** In a tenth aspect of the present invention, there are provided iron oxide hydroxide composite particles having an average particle diameter of from 0.1 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coat formed on at least a part of the surface of the iron oxide hydroxide particles, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon;  
a coating formed on surface of the said coat, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic red-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0031]** In an eleventh aspect of the present invention, there is provided a pigment comprising iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0032]** In a twelfth aspect of the present invention, there is provided a pigment comprising iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coat formed on at least a part of the surface of the iron oxide hydroxide particles, comprising at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon;  
a coating formed on surface of the said coat, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0033]** In a thirteenth aspect of the present invention, there is provided a green-based pigment comprising iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic blue-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 5 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0034]** In fourteenth aspect of the present invention, there is provided an orange-based pigment comprising iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic red-based pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0035]** In a fifteenth aspect of the present invention, there is provided a paint comprising:

a paint base material, and  
a pigment comprising iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0036]** In a sixteenth aspect of the present invention, there is provided a rubber or resin composition comprising:

a base material for rubber or resin composition, and  
a pigment comprising iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , comprising:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of the iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic pigment coat formed on the coating layer comprising the organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

**[0037]** First, the pigment such as green or orange-based pigment according to the present invention will be explained below.

**[0038]** The pigment of the present invention is composed of iron oxide hydroxide composite particles which comprise iron oxide hydroxide particles as core particles, a coating layer of organosilicon compounds formed on the surface of the core particle, and an organic blue-based pigment or an organic red-based pigment adhered on the coating layer, and have an average major axial diameter of from 0.005 to 1.0  $\mu\text{m}$ .

**[0039]** The above iron oxide hydroxide composite particles of the present invention are generally classified into:

- (1) iron oxide hydroxide composite particles comprising iron oxide hydroxide particles as core particles, a coating layer of organosilicon compounds formed on the surface of the core particle, and an organic blue-based pigment or an organic red-based pigment adhered on the coating layer, and having an average major axial diameter of 0.1 to 1.0  $\mu\text{m}$ ; and
- (2) fine iron oxide hydroxide composite particles comprising fine iron oxide hydroxide particles as core particles, a coating layer of organosilicon compounds formed on the surface of the core particle, and an organic blue-based pigment or an organic red-based pigment adhered on the coating layer, and having an average major axial diameter of from 0.005 to less than 0.1  $\mu\text{m}$ .

**[0040]** The iron oxide hydroxide particles used as core particles in the present invention are of an acicular shape or a rectangular shape. The "acicular" shape used herein may include a spindle shape and a rice-ball shape in addition to literally acicular or needle-like shape.

**[0041]** The iron oxide hydroxide particles used in the present invention include goethite ( $\alpha\text{-FeOOH}$ ) particles and lepidocrocite ( $\gamma\text{-FeOOH}$ ) particles. In the consideration of heat resistance of the obtained pigments, iron oxide hydroxide particles obtained by subjecting iron oxide hydroxide particles to heat resistance-imparting treatments is preferred. More specifically, the preferred iron oxide hydroxide particles used as core particles in the present invention may include iron oxide hydroxide particles whose surfaces are coated with at least one compound selected from the group consisting of hydroxides of aluminum and oxides of aluminum; iron oxide hydroxide particles containing aluminum inside thereof; iron oxide hydroxide particles having a coating layer composed of an iron and aluminum oxide hydroxide composite on the surface thereof; and iron oxide hydroxide particles subjected to any two or more of the above heat resistance-imparting treatments.

**[0042]** In the case of the iron oxide hydroxide particles whose surfaces are coated with at least one compound selected from the group consisting of hydroxides of aluminum and oxides of aluminum, the aluminum content thereof is 0.1 to 20.0% by weight (calculated as Al) based on the weight of the iron oxide hydroxide particles coated. In the

case of the iron oxide hydroxide particles containing aluminum inside thereof, the aluminum content thereof is 0.05 to 50% by weight (calculated as Al) based on the weight of the iron oxide hydroxide particles containing aluminum inside thereof. In the case of the iron oxide hydroxide particles having a coating layer composed of an iron and aluminum oxide hydroxide composite on the surfaces thereof, the aluminum content thereof is 0.1 to 10% by weight (calculated as Al) based on the weight of the iron oxide hydroxide particles, and the iron content thereof is 0.1 to 30% by weight (calculated as Fe) based on the weight of the iron oxide hydroxide particles.

**[0043]** The iron oxide hydroxide particles used in the present invention have an average major axial diameter of 0.005 to 1.0  $\mu\text{m}$ ; an average minor axial diameter of 0.0025 to 0.5  $\mu\text{m}$ ; an aspect ratio of 2:1 to 20:1; a BET specific surface area value of 5 to 300  $\text{m}^2/\text{g}$ ; and a geometrical standard deviation of major axial diameters of 1.01 to 2.0. As to the hue of the iron oxide hydroxide particles, the  $L^*$  value thereof is 40 to 80; the  $a^*$  value thereof is -57.7 to +57.7 ( $a^*$  value  $\neq 0$ ); and the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is from more than  $60^\circ$  to less than  $120^\circ$ .

**[0044]** More specifically, the following two kinds of iron oxide hydroxide particles as classified based on average major axial diameter thereof, are individually explained.

(1) In the case of iron oxide hydroxide particles having an average major axial diameter of 0.1 to 1.0  $\mu\text{m}$ :

**[0045]** The average major axial diameter of the iron oxide hydroxide particles (1) is usually 0.1 to 1.0  $\mu\text{m}$ , preferably 0.15 to 0.9  $\mu\text{m}$ .

**[0046]** When the average major axial diameter is more than 1.0  $\mu\text{m}$ , the obtained pigments become coarse particles, resulting in deteriorated tinting strength.

**[0047]** The average minor axial diameter of the iron oxide hydroxide particles (1) is usually 0.05 to 0.5  $\mu\text{m}$ , preferably 0.075 to 0.45  $\mu\text{m}$ .

**[0048]** The aspect ratio (ratio of average major axial diameter to average minor axial diameter; hereinafter referred to merely as "aspect ratio") is usually not more than 20:1, preferably 2:1 to 15:1.

**[0049]** When the aspect ratio is more than 20:1, the particles may tend to be entangled or interlaced with each other, so that it may be difficult to uniformly form a coating layer of organosilicon compounds on the surface of each iron oxide hydroxide particle and uniformly adhere the organic pigment thereonto.

**[0050]** The geometrical standard deviation value of major axial diameters is usually not more than 2.0, preferably not more than 1.8, more preferably not more than 1.6.

**[0051]** When the geometrical standard deviation value is more than 2.0, a large amount of coarse particles may be present, so that the particles may be inhibited from being uniformly dispersed. As a result, it may be difficult to uniformly form a coating layer of organosilicon compounds on the surface of each iron oxide hydroxide particle and uniformly adhere the organic pigment thereonto. The lower limit of the geometrical standard deviation value is 1.01. It is difficult to industrially produce iron oxide hydroxide particles having a geometrical standard deviation value of less than 1.01.

**[0052]** The BET specific surface area value is usually 5 to 150  $\text{m}^2/\text{g}$ , preferably 10 to 120  $\text{m}^2/\text{g}$ , more preferably 15 to 100  $\text{m}^2/\text{g}$ .

**[0053]** When the BET specific surface area value is less than 5  $\text{m}^2/\text{g}$ , the iron oxide hydroxide particles may become coarse or tend to be sintered together. As a result, the obtained particles may become coarse, resulting in deteriorated tinting strength.

**[0054]** As to the hue of the iron oxide hydroxide particles (1), the  $L^*$  value thereof is 40 to 80; the  $a^*$  value thereof is -57.7 to +57.7 ( $a^*$  value  $\neq 0$ ); the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is from more than  $60^\circ$  to less than  $120^\circ$ . When any of the  $L^*$ ,  $a^*$ ,  $b^*$  and  $h$  values is out of the above specified range, the aimed pigments such as green or orange-based pigments according to the present invention may not be obtained.

(2) In the case of iron oxide hydroxide fine particles having an average major axial diameter of from 0.005  $\mu\text{m}$  to less than 0.1  $\mu\text{m}$ :

**[0055]** The average major axial diameter thereof is usually from 0.005  $\mu\text{m}$  to less than 0.1  $\mu\text{m}$ . When the average major axial diameter is less than 0.005  $\mu\text{m}$ , the particles may tend to be agglomerated together due to increase in intermolecular force therebetween. As a result, it may be difficult to uniformly form a coating layer of organosilicon compounds on the surface of each iron oxide hydroxide fine particle and uniformly adhere the organic pigment thereonto.

**[0056]** In the consideration of uniform formation of the coating layer of organosilicon compounds on the surface of each iron oxide hydroxide fine particle, uniform adhesion of the organic pigment thereonto, and the average major axial diameter is preferably 0.008 to 0.096  $\mu\text{m}$ , more preferably 0.01 to 0.092.

**[0057]** The average minor axial diameter thereof is usually from 0.0025 to less than 0.05  $\mu\text{m}$ , preferably 0.004 to 0.048  $\mu\text{m}$ , more preferably 0.005 to 0.046  $\mu\text{m}$ ; the aspect ratio thereof is usually not more than 20:1, preferably not

more than 15:1, more preferably not more than 10:1 (lower limit of the aspect ratio: 2:1); the BET specific surface area value thereof is usually 50 to 300 m<sup>2</sup>/g, preferably 70 to 280 m<sup>2</sup>/g, more preferably 80 to 250 m<sup>2</sup>/g; and the geometrical standard deviation value of major axial diameters thereof is usually not more than 2.0, preferably not more than 1.8, more preferably not more than 1.6 (lower limit of the geometrical standard deviation value: 1.01).

**[0058]** When the average minor axial diameter is less than 0.0025 μm, the intermolecular force between the particles may become large due to fineness thereof, so that it may become difficult to uniformly form a coating layer of organo-silicon compounds on the surface of each iron oxide hydroxide fine particle and uniformly adhere the organic pigment thereonto.

**[0059]** When the BET specific surface area value is more than 300 m<sup>2</sup>/g, the intermolecular force between the particles may become large due to fineness thereof, so that it may be difficult to uniformly form a coating layer of organo-silicon compounds on the surface of each iron oxide hydroxide fine particle and uniformly adhere the organic pigment thereonto.

**[0060]** As to the hue of the iron oxide hydroxide fine particles (2) used in the present invention, the L\* value thereof is 40 to 80; the a\* value thereof is -57.7 to +57.7 (a\* value ≠ 0); the b\* value thereof is from more than +100; and the h value thereof is from more than 60° to less than 120°. When any of the L\*, a\* and b\* values is out of the above specified range, the aimed fine pigments such as green or orange-based fine pigments according to the present invention may not be obtained.

**[0061]** The iron oxide hydroxide fine particles (2) used in the present invention have a hiding power of preferably less than 600 cm<sup>2</sup>/g, more preferably not more than 500 cm<sup>2</sup>/g. When the hiding power is not less than 600 cm<sup>2</sup>/g, the fine pigments obtained using the iron oxide hydroxide fine particles as core particles may show a too high hiding power.

**[0062]** As to the chemical resistances of the iron oxide hydroxide fine particles (2) used in the present invention, the acid resistance (ΔE\*) thereof is preferably not more than 3.0, more preferably not more than 2.5; and the alkali resistance (ΔE\*) thereof is preferably not more than 3.0, more preferably not more than 2.5, when measured by the evaluation methods described hereinafter. When any of the acid and alkali resistances (ΔE\*) is more than 3.0, it may be difficult to obtain the aimed fine pigments such as green or orange-based fine pigments having excellent chemical resistances according to the present invention.

**[0063]** As to the heat resistance of the iron oxide hydroxide particles used in the present invention, the heat resistance temperature thereof is preferably not less than 180°C, more preferably not less than 185°C. In the consideration of the heat resistance of the obtained pigments such as green or orange-based pigments, the use of iron oxide hydroxide particles subjected to heat resistance-imparting treatments is preferred. In the case of the iron oxide hydroxide particles whose surfaces are coated with at least one compound selected from the group consisting of hydroxides of aluminum and oxides of aluminum, the heat resistance temperature thereof is about 240°C. In the case of the iron oxide hydroxide particles containing aluminum inside thereof, the heat resistance temperature thereof is about 245°C. Also, in the case of the iron oxide hydroxide particles having a coating layer composed of an aluminum and iron oxide hydroxide composite on the surfaces thereof, the heat resistance temperature thereof is about 250°C.

**[0064]** The coating formed on the surface of the core particle comprises at least one organosilicon compound selected from the group consisting of (1) organosilane compounds obtainable from alkoxysilane compounds; and (2) polysiloxanes and modified polysiloxanes selected from the group consisting of (2-A) polysiloxanes modified with at least one compound selected from the group consisting of polyethers, polyesters and epoxy compounds (hereinafter referred to merely as "modified polysiloxanes"), and (2-B) polysiloxanes whose molecular terminal is modified with at least one group selected from the group consisting of carboxylic acid groups, alcohol groups and a hydroxyl group (hereinafter referred to merely as "terminal-modified polysiloxanes").

**[0065]** The organosilane compounds (1) may be produced by drying or heat-treating alkoxysilane compounds represented by the formula (I):



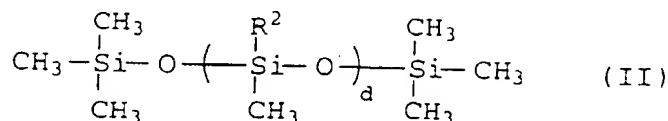
wherein R<sup>1</sup> is C<sub>6</sub>H<sub>5</sub>-, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>- or n-C<sub>b</sub>H<sub>2b+1</sub>- (wherein b is an integer of 1 to 18); X is CH<sub>3</sub>O- or C<sub>2</sub>H<sub>5</sub>O-; and a is an integer of 0 to 3.

**[0066]** The drying or heat-treatment of the alkoxysilane compounds may be conducted, for example, at a temperature of usually 40 to 200°C, preferably 60 to 150°C for usually 10 minutes to 12 hours, preferably 30 minutes to 3 hours.

**[0067]** Specific examples of the alkoxysilane compounds may include methyltriethoxysilane, dimethyldiethoxysilane, phenyltriethoxysilane, diphenyldiethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane, isobutyltrimethoxysilane, decyltrimethoxysilane or the like. Among these alkoxysilane compounds, in view of the desorption percentage and the adhering effect of organic pigments, methyltriethoxysilane, phenyltriethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane and isobutyltrimethoxysilane are preferred,

and methyltriethoxysilane and methyltrimethoxysilane are more preferred.

[0068] As the polysiloxanes (2), there may be used those compounds represented by the formula (II):

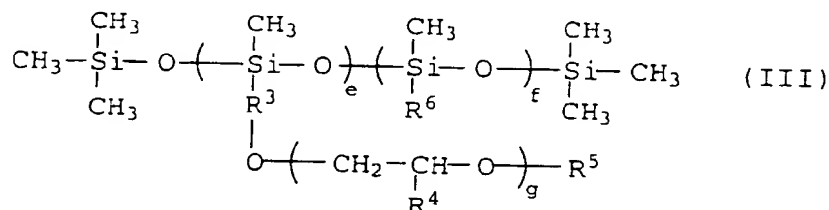


wherein  $\text{R}^2$  is H- or  $\text{CH}_3$ -, and d is an integer of 15 to 450.

[0069] Among these polysiloxanes, in view of the desorption percentage and the adhering effect of the organic pigments, polysiloxanes having methyl hydrogen siloxane units are preferred.

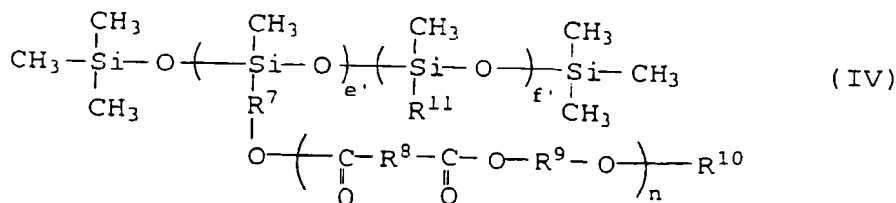
[0070] As the modified polysiloxanes (2-A), there may be used:

(a) polysiloxanes modified with polyethers represented by the formula (III):



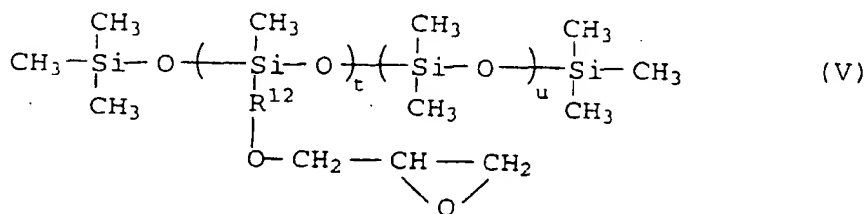
wherein  $\text{R}^3$  is  $-(\text{CH}_2)_h-$ ;  $\text{R}^4$  is  $-(\text{CH}_2)_i-\text{CH}_3$ ;  $\text{R}^5$  is  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{C}(\text{CH}_3)=\text{CH}_2$  or  $-(\text{CH}_2)_j-\text{CH}_3$ ;  $\text{R}^6$  is  $-(\text{CH}_2)_k-\text{CH}_3$ ; g and h are an integer of 1 to 15; i, j and k are an integer of 0 to 15; e is an integer of 1 to 50; and f is an integer of 1 to 300;

(b) polysiloxanes modified with polyesters represented by the formula (IV):



wherein  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  are  $-(\text{CH}_2)_q-$  and may be the same or different;  $\text{R}^{10}$  is  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{C}(\text{CH}_3)=\text{CH}_2$  or  $-(\text{CH}_2)_r-\text{CH}_3$ ;  $\text{R}^{11}$  is  $-(\text{CH}_2)_s-\text{CH}_3$ ; n and q are an integer of 1 to 15; r and s are an integer of 0 to 15;  $e'$  is an integer of 1 to 50; and  $f'$  is an integer of 1 to 300;

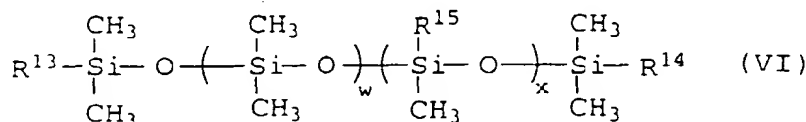
(c) polysiloxanes modified with epoxy compounds represented by the formula (V):



wherein R<sup>12</sup> is  $-(\text{CH}_2)_v-$ ; v is an integer of 1 to 15; t is an integer of 1 to 50; and u is an integer of 1 to 300; or a mixture thereof.

[0071] Among these modified polysiloxanes (2-A), in view of the desorption percentage and the adhering effect of the organic pigments, the polysiloxanes modified with the polyethers represented by the formula (III), are preferred.

[0072] As the terminal-modified polysiloxanes (2-B), there may be used those represented by the formula (VI):



wherein R<sup>13</sup> and R<sup>14</sup> are -OH, R<sup>16</sup>OH or R<sup>17</sup>COOH and may be the same or different; R<sup>15</sup> is -CH<sub>3</sub> or -C<sub>6</sub>H<sub>5</sub>; R<sup>16</sup> and R<sup>17</sup> are  $-(\text{CH}_2)_y-$ ; y is an integer of 1 to 15; w is an integer of 1 to 200; and x is an integer of 0 to 100.

[0073] Among these terminal-modified polysiloxanes, in view of the desorption percentage and the adhering effect of the organic pigments, the polysiloxanes whose terminals are modified with carboxylic acid groups are preferred.

[0074] The coating amount of the organosilicon compounds is usually 0.02 to 5.0 % by weight, preferably 0.03 to 4.0 % by weight, more preferably 0.05 to 3.0 % by weight (calculated as Si) based on the weight of the iron oxide hydroxide particles coated with the organosilicon compounds.

[0075] When the coating amount of the organosilicon compounds is less than 0.02 % by weight, it may be difficult to adhere the organic pigments in a predetermined.

[0076] When the coating amount of the organosilicon compounds is more than 5.0 % by weight, the organic pigments can be adhered in a predetermined. Therefore, it is unnecessary and meaningless to coat the core particles with such a large amount of the organosilicon compounds.

[0077] As to the organic pigments used in the present invention, organic blue-based pigments and organic red-based pigments may be exemplified. The amount of the organic pigment such as organic blue-based pigments and organic red-based pigments adhered on the coating layer composed of organosilicon compounds is usually 1 to 30 parts based on 100 parts by weight of the iron oxide hydroxide particles.

[0078] As the organic blue-based pigments used in the present invention, there may be used phthalocyanine-based pigments such as metal-free phthalocyanine blue, phthalocyanine blue (copper phthalocyanine) and fast sky blue (sulfonated copper phthalocyanine), and alkali blue pigments, or the like. In the consideration of the hue of the obtained green-based fine pigments, among these pigments, the use of phthalocyanine blue is preferred.

[0079] In particular, in the consideration of light resistance, the use of low-chlorinated copper phthalocyanine, NC-type (non-crystallization-type) copper phthalocyanine or NC-type low-chlorinated copper phthalocyanine is preferred.

[0080] The amount of the organic blue-based pigment adhered is preferably 5 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

[0081] When the amount of the organic blue-based pigment adhered is out of the above-mentioned range, it may be difficult to obtain the aimed green-based pigment of the present invention. The amount of the organic blue-based pigment adhered is more preferably 7.5 to 25 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

[0082] As the organic red-based pigments used in the present invention, there may be used quinacridone-based pigments such as quinacridone red, azo-based pigments such as permanent red, condensed azo-based pigments such as condensed azo red, and perylene-based pigments such as perylene red. In the consideration of heat resistance and light resistance of the obtained orange-based pigments, the use of quinacridone-based pigments is preferred.

[0083] The amount of the organic red-based pigment adhered is usually 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles. When the amount of the organic red-based pigment adhered is less than 1 part by weight or more than 30 parts by weight, it may be difficult to obtain the aimed orange-based pigment of the present invention. The amount of the organic red-based pigment adhered is preferably 3 to 25 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles.

[0084] The shape and size of the green or orange-based pigments of the present invention considerably varies depending upon those of the iron oxide hydroxide particles as core particles, and usually have an analogous configuration to that of the iron oxide hydroxide particles.

[0085] For example, the green or orange-based pigment according to the present invention has an average major axial diameter of 0.005 to 1.0  $\mu\text{m}$ ; an average minor axial diameter of 0.0025 to 0.5  $\mu\text{m}$ ; an aspect ratio of 2.0:1 to 20:1; a BET specific surface area value of 6 to 300  $\text{m}^2/\text{g}$ ; a geometrical standard deviation value of major axial diameters

of 1.01 to 2.0; and a desorption percentage of the organic pigment of not more than 15 %. As to the heat resistance of the green or orange-based pigment, the heat resistance temperature thereof is higher by +5 to +40° than that of the iron oxide hydroxide particles. As to the chemical resistances of the green or orange-based pigment, the acid resistance ( $\Delta E^*$  value) thereof is not more than 1.5, and the alkali resistance thereof is not more than 1.5, when evaluated by the method specified hereinafter.

[0086] Next, the properties of the green or orange-based pigments used on the present invention are more concretely explained as follows.

(1) In the case where iron oxide hydroxide particles having an average major axial diameter of 0.1 to 1.0  $\mu\text{m}$  are used as core particles:

[0087] The green or orange-based pigment according to the present invention has an average major axial diameter of usually 0.1 to 1.0  $\mu\text{m}$ , preferably 0.15 to 0.9  $\mu\text{m}$ .

[0088] When the average major axial diameter of the green or orange-based pigment is more than 1.0  $\mu\text{m}$ , the pigment particles may be larger, resulting in deteriorated tinting strength.

[0089] The green or orange-based pigment according to the present invention is of an acicular or rectangular shape.

[0090] The green or orange-based pigment according to the present invention has an aspect ratio of usually not more than 20:1, preferably 2:1 to 15:1, more preferably 2:1 to 10:1. When the aspect ratio of the green or orange-based pigment is more than 20:1, the pigment particles may tend to be entangled or interlaced with each other, resulting in poor dispersibility in vehicles or resin compositions as well as increased viscosity of the coating solution.

[0091] The green or orange-based pigment according to the present invention suitably has a geometrical standard deviation value of particle sizes of not more than 2.0. When the geometrical standard deviation value of particle sizes of the green or orange-based pigment is more than 2.0, a considerable amount of coarse particles are present, so that it may be difficult to uniformly disperse the pigment in vehicles or resin compositions. In the consideration of uniform dispersion in vehicles or resin compositions, the geometrical standard deviation value of particle sizes of the green or orange-based pigment is preferably not more than 1.8, more preferably not more than 1.6. In the consideration of industrial productivity, the lower limit of the geometrical standard deviation value of particle sizes of the green or orange-based pigment is 1.01, since it is difficult to industrially produce those pigments having a geometrical standard deviation value of less than 1.01.

[0092] The green or orange-based pigment according to the present invention has a BET specific surface area value of usually 6 to 160  $\text{m}^2/\text{g}$ , preferably 11 to 130  $\text{m}^2/\text{g}$ , more preferably 16 to 110  $\text{m}^2/\text{g}$ . When the BET specific surface area value of the green or orange-based pigment is less than 6  $\text{m}^2/\text{g}$ , the obtained green or orange-based pigment particles may be coarser, resulting in deteriorated tinting strength.

[0093] The green or orange-based pigment according to the present invention has a desorption percentage of the organic pigment of preferably not more than 15%, more preferably not more than 12%. When the desorption percentage of the organic pigment is more than 15%, the pigment particles may tend to be inhibited from being uniformly dispersed in vehicles or resin compositions due to desorbed organic pigment particles. Further, a portion of the surface of the iron oxide hydroxide core particle from which the organic pigment is desorbed, is exposed to outside, so that the obtained iron oxide hydroxide composite particles fail to exhibit a uniform hue.

[0094] Especially, as to the hue of the green-based pigment according to the present invention, the  $L^*$  value thereof is 25 to 80; the  $a^*$  value thereof is from -100 to less than 0; the  $b^*$  value thereof is -100 to +100; and the  $h$  value thereof is 120° to 240°.

[0095] In addition, as to the hue of the orange-based pigment according to the present invention, the  $L^*$  value thereof is 25 to 80; the  $a^*$  value thereof is from more than 0 to +100; the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is 30° to 60°.

[0096] As to the heat resistance of the green or orange-based pigment according to the present invention, the heat resistance temperature thereof is higher by +5 to +40° than that of the iron oxide hydroxide particles as core particles.

[0097] The green or orange-based pigment according to the present invention has a tinting strength of preferably not less than 115%, more preferably not less than 120%, when measured by the evaluation method specified herein-after.

[0098] The green or orange-based pigment according to the present invention has a hiding power of preferably not less than 1,750  $\text{cm}^2/\text{g}$ , more preferably not less than 1,800  $\text{cm}^2/\text{g}$ , when measured by the evaluation method specified hereinafter.

[0099] As to the chemical resistances of the green or orange-based pigment according to the present invention, the acid resistance ( $\Delta E^*$  value) thereof is preferably not more than 1.5, more preferably not more than 1.2; and the alkali resistance ( $\Delta E^*$  value) thereof is preferably not more than 1.5, more preferably not more than 1.2, when measured by the evaluation method specified hereinafter.



(2) In the case where iron oxide hydroxide particles having an average major axial diameter of from 0.005  $\mu\text{m}$  to less than 0.1  $\mu\text{m}$  are used as core particles:

**[0100]** The green or orange-based fine pigment of the present invention has an average major axial diameter of from usually 0.005  $\mu\text{m}$  to less than 0.1  $\mu\text{m}$ , preferably 0.008 to 0.096  $\mu\text{m}$ , more preferably 0.01 to 0.092  $\mu\text{m}$ .

**[0101]** When the average major axial diameter of the green or orange-based fine pigment is less than 0.005  $\mu\text{m}$ , the intermolecular force between the pigment particles may be increased due to fineness thereof, so that the particles may tend to be agglomerated together, resulting in poor dispersibility in vehicles or resin compositions.

**[0102]** The green or orange-based fine pigment of the present invention is also of an acicular or rectangular shape.

**[0103]** The green or orange-based fine pigment of the present invention has an aspect ratio of preferably not more than 20:1, more preferably 2:1 to 15:1, still more preferably 2:1 to 10:1. When the aspect ratio of the green or orange-based pigment is more than 20:1, the pigment particles may tend to be entangled or interlaced with each other, resulting in poor dispersibility in vehicles or resin compositions as well as increased viscosity of the obtained coating solution.

**[0104]** The green or orange-based fine pigment according to the present invention has an average minor axial diameter of usually from 0.0025  $\mu\text{m}$  to less than 0.05  $\mu\text{m}$ , preferably 0.004 to 0.048  $\mu\text{m}$ , more preferably 0.005 to 0.046  $\mu\text{m}$ . When the average minor axial diameter of the green or orange-based fine pigment is less than 0.0025  $\mu\text{m}$ , the intermolecular force between the pigment particles may be increased due to fineness thereof, so that the particles may tend to be agglomerated together, resulting in poor dispersibility in vehicles or resin compositions.

**[0105]** The green or orange-based fine pigment according to the present invention suitably has a geometrical standard deviation value of particle sizes of usually not more than 2.0. When the geometrical standard deviation value of particle sizes of the green or orange-based fine pigment is more than 2.0, a considerable amount of coarse particles may be present, so that it may be difficult to uniformly disperse the fine pigment particles in vehicles or resin compositions. In the consideration of uniform dispersion in vehicles or resin compositions, the geometrical standard deviation value of particle sizes of the green or orange-based fine pigment is preferably not more than 1.8, more preferably not more than 1.6. In the consideration of industrial productivity, the lower limit of the geometrical standard deviation value of particle sizes of the green or orange-based fine pigment is 1.01, since it is difficult to industrially produce those pigments having a geometrical standard deviation value of less than 1.01.

**[0106]** The green or orange-based fine pigment according to the present invention has a BET specific surface area value of usually 50 to 300  $\text{m}^2/\text{g}$ , preferably 70 to 280  $\text{m}^2/\text{g}$ , more preferably 80 to 250  $\text{m}^2/\text{g}$ . When the BET specific surface area value of the green or orange-based fine pigment is less than 50  $\text{m}^2/\text{g}$ , the obtained green or orange-based fine pigment particles may be coarser, resulting in too high hiding power. As a result, coating films or resin compositions obtained using the green or orange-based fine pigment may fail to exhibit a sufficient transparency. On the other hand, when the BET specific surface area value of the green or orange-based fine pigment is more than 300  $\text{m}^2/\text{g}$ , the intermolecular force between the fine pigment particles may be increased due to fineness thereof, so that the particles may tend to be agglomerated together, resulting in poor dispersibility in vehicles or resin compositions.

**[0107]** The organic pigment constituting the green or orange-based fine pigment according to the present invention has a desorption percentage of the organic pigment of usually not more than 15 %, preferably not more than 12 %. When the desorption percentage of the organic pigment is more than 15 %, the fine pigment particles tends to be inhibited from being uniformly dispersed in vehicles or resin compositions due to desorbed organic pigment particles. Further, a portion of the surface of the iron oxide hydroxide fine particles as core particle from which the organic pigment particles are desorbed, is exposed to outside, so that the obtained iron oxide hydroxide composite fine particles fail to exhibit a uniform hue.

**[0108]** Especially, as to the hue of the green-based fine pigment according to the present invention, the  $L^*$  value thereof is usually 25 to 80; the  $a^*$  value thereof is usually from -100 to less than 0; the  $b^*$  value thereof is -100 to +100; and the  $h$  value thereof is usually 120 to 240°.

**[0109]** In addition, as to the hue of the orange-based fine pigment according to the present invention, the  $L^*$  value thereof is usually 25 to 80; the  $a^*$  value thereof is usually from more than 0 to +100; the  $b^*$  value thereof is usually from more than 0 to +100; and the  $h$  value thereof is usually from 30° to 60°.

**[0110]** As to the heat resistance of the green or orange-based fine pigment according to the present invention, the heat resistance temperature thereof is usually higher by +5 to +40° than that of the iron oxide hydroxide fine particles as core particles, and is preferably not less than 210°C, more preferably not less than 215°C.

**[0111]** The green or orange-based fine pigment according to the present invention has a tinting strength of preferably not less than 115 %, more preferably not less than 120 %, when measured by the evaluation method specified hereinafter.

**[0112]** The green or orange-based fine pigment according to the present invention has a hiding power of preferably less than 600  $\text{cm}^2/\text{g}$ , more preferably not more than 500  $\text{cm}^2/\text{g}$ . When the hiding power of the green or orange-based fine pigment is not less than 600  $\text{cm}^2/\text{g}$ , coating films or resin compositions obtained using the green or orange-based fine pigment may fail to exhibit a sufficient transparency due to a too high hiding power thereof.

[0113] As to the chemical resistances of the green or orange-based fine pigment according to the present invention, the acid resistance ( $\Delta E^*$  value) thereof is preferably not more than 1.5, more preferably not more than 1.3; and the alkali resistance ( $\Delta E^*$  value) thereof is preferably not more than 1.5, more preferably not more than 1.3, when measured by the evaluation method specified hereinafter.

[0114] Before forming the coating layer comprising the organosilicon compound onto the iron oxide hydroxide particles, the surfaces of the core particles may be preliminarily coated with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon (hereinafter referred to merely as "hydroxides and/or oxides of aluminum and/or silicon"). When the coating layer is formed on the surfaces of the core particles, the desorption percentage of the organic pigment from the surfaces of the iron oxide hydroxide particles can be reduced as compared to those having no coating layer, and the heat resistance of the obtained composite particles can be slightly increased.

[0115] The total coating amount of the hydroxides and/or oxides of aluminum and/or silicon is 0.01 to 20% by weight (calculated as Al, Si or a sum of Al and Si) based on the weight of the coated iron oxide hydroxide particles.

[0116] When the coating amount of the hydroxides and/or oxides of aluminum and/or silicon is less than 0.01% by weight, the effect of reducing the desorption percentage of the organic pigment may not be obtained. Since a sufficient effect of reducing the desorption percentage of the organic pigment can be obtained by adjusting the coating amount of the hydroxides and/or oxides of aluminum and/or silicon to 0.01 to 20% by weight, it is unnecessary and meaningless to coat the core particles with the hydroxides and/or oxides of aluminum and/or silicon in an amount of more than 20% by weight.

[0117] The green or orange-based pigment in which the iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon are used as core particles, are substantially identical in particle size, geometrical standard deviation value, BET specific surface area value, hue, tinting strength, hiding power and chemical resistances to those used for the core particles having no coating layer composed of the hydroxides and/or oxides of aluminum and/or silicon. Also, by forming such a coating layer composed of the hydroxides and/or oxides of aluminum and/or silicon on the core particles, the desorption percentage of the organic pigment is improved, i.e., can be reduced to preferably not more than 12 %, more preferably not more than 10 %, and the heat resistance of the obtained composite particles becomes higher by +5 to +30°C than those obtained by using the core particles having no coating layer composed of the hydroxides and/or oxides of aluminum and/or silicon.

[0118] Next, the paint containing the green or orange-based pigment according to the present invention, is described.

[0119] The paint containing the green or orange-based pigment according to the present invention has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, a gloss of 70 to 115 % (in a coating film), a heat resistance temperature of usually not less than 220°C (in a coating film), an acid resistance ( $\Delta G$  value) as a chemical resistances of usually not more than 12 % (in a coating film), an alkali resistance ( $\Delta G$  value) as a chemical resistances of usually not more than 12 % (in a coating film), and a  $L^*$  value of usually 25 to 85 (in a coating film).

(A) Paint containing the green-based pigment having an average major axial diameter of 0.1 to 1.0  $\mu\text{m}$ :

[0120] The paint containing the green-based pigment according to the present invention has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.2. When a coating film is produced by using the solvent-based paints, the gloss of the coating film is usually 75 to 110 %, preferably 80 to 110 %; and the heat resistance temperature of the coating film is usually not less than 240°C, preferably not less than 245°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from -100 to less than 0; the  $b^*$  value thereof is -100 to +100; and the  $h$  value thereof is usually 120 to 240°.

[0121] The paint containing the green-based pigment obtained by using the core particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.2. When a coating film is produced by using the solvent-based paints, the gloss of the coating film is usually 80 to 115 %, preferably 85 to 115 %; and the heat resistance temperature of the coating film is usually not less than 245°C, preferably not less than 250°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from -100 to less than 0; the  $b^*$  value thereof is -100 to +100; and the  $h$  value thereof is usually 120 to 240°.

[0122] The water-based paint containing the green-based pigment according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.2. When a coating film is produced by using the water-based paints, the gloss of the coating film is usually 70 to 110 %, preferably 75 to 110 %; and the heat

resistance temperature of the coating film is usually not less than 235°C, preferably not less than 240°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the water-based paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from -100 to less than 0; the  $b^*$  value thereof is -100 to +100; and the  $h$  value thereof is usually 120 to 240°.

**[0123]** The water-based paint containing the green-based pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.2. When a coating film is produced by using the water-based paints, the gloss of the coating film is usually 75 to 115 %, preferably 80 to 115 %; and the heat resistance temperature of the coating film is usually not less than 240°C, preferably not less than 245°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the water-based paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from -100 to less than 0; the  $b^*$  value thereof is -100 to +100; and the  $h$  value thereof is usually 120 to 240°.

(B) Paint containing the orange-based pigment having an average major axial diameter of 0.1 to 1.0  $\mu\text{m}$ :

**[0124]** The paint containing the orange-based pigment according to the present invention has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.2. When a coating film is produced by using the solvent-based paints, the gloss of the coating film is usually 75 to 110 %, preferably 80 to 110 %; and the heat resistance temperature of the coating film is usually not less than 240°C, preferably not less than 245°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from more than 0 to +100; the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is 30 to 60°.

**[0125]** The paint containing the orange-based pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.2. When a coating film is produced by using the solvent-based paints, the gloss of the coating film is usually 80 to 115 %, preferably 85 to 115 %; and the heat resistance temperature of the coating film is usually not less than 245°C, preferably not less than 250°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from more than 0 to +100; the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is 30 to 60°.

**[0126]** The water-based paint containing the orange-based pigment according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.2. When a coating film is produced by using the water-based paints, the gloss of the coating film is usually 70 to 110%, preferably 75 to 110%; and the heat resistance temperature of the coating film is usually not less than 235°C, preferably not less than 240°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the water-based paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from more than 0 to +100; the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is 30 to 60°.

**[0127]** The water-based paint containing the orange-based pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.2. When a coating film is produced by using the water-based paints, the gloss of the coating film is usually 75 to 115 %, preferably 80 to 115 %; and the heat resistance temperature of the coating film is usually not less than 240°C, preferably not less than 245°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the water-based paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from more than 0 to +100; the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is 30 to 60°.

(C) Paint containing the green-based fine pigment having an average major axial diameter of from 0.005 to less than 0.1  $\mu\text{m}$ :

**[0128]** The paint containing the green-based fine pigment according to the present invention has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.3. When a coating film is produced by using the solvent-based paints, the gloss of the coating film is usually 75 to 110 %, preferably 80 to 110 %; and the heat resistance temperature of the coating film is usually not less than 220°C, preferably not less than 225°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, more preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from -100 to less than 0; and the  $b^*$  value thereof is -100 to +100; and the  $h$  value thereof is 120 to 240°. As to the transparency of the coating film, the linear absorption thereof is preferably not more than 0.05  $\mu\text{m}^{-1}$ .

**[0129]** The paint containing the green-based fine pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.3. When a coating film is produced by using the solvent-based paints, the gloss of the coating film is usually 80 to 115 %, preferably 85 to 115 %; and the heat resistance temperature of the coating film is usually not less than 230°C, preferably not less than 235°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from -100 to less than 0; the  $b^*$  value thereof is -100 to +100; and the  $h$  value thereof is 120 to 240°. As to the transparency of the coating film, the linear absorption thereof is preferably not more than 0.05  $\mu\text{m}^{-1}$ .

**[0130]** The water-based paint containing the green-based fine pigment according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.3. When a coating film is produced by using the water-based paints, the gloss of the coating film is usually 70 to 110 %, preferably 75 to 110 %; and the heat resistance temperature of the coating film is usually not less than 220°C, preferably not less than 225°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the water-based paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from -100 to less than 0; and the  $b^*$  value thereof is -100 to +100. As to the transparency of the coating film, the linear absorption thereof is preferably not more than 0.05  $\mu\text{m}^{-1}$ .

**[0131]** The water-based paint containing the green-based fine pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.3. When a coating film is produced by using the water-based paints, the gloss of the coating film is usually 75 to 115 %, preferably 80 to 115 %; and the heat resistance temperature of the coating film is usually not less than 230°C, preferably not less than 235°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the water-based paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from -100 to less than 0; and the  $b^*$  value thereof is -100 to +100; and the  $h$  value thereof is 120 to 240°. As to the transparency of the coating film, the linear absorption thereof is preferably not more than 0.05  $\mu\text{m}^{-1}$ .

(D) Paint containing the orange-based fine pigment having an average major axial diameter of from 0.005  $\mu\text{m}$  to less than 0.1  $\mu\text{m}$ :

**[0132]** The paint containing the orange-based fine pigment according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.3. When a coating film is produced by using the solvent-based paints, the gloss of the coating film is usually 75 to 110 %, preferably 80 to 110 %; and the heat resistance temperature of the coating film is usually not less than 220°C, preferably not less than 225°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from more than 0 to +100; the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is 30 to 60°. As to the transparency of the coating film, the linear absorption thereof is preferably not more than 0.05  $\mu\text{m}^{-1}$ .

**[0133]** The paint containing the orange-based fine pigment obtained by using as the core particles iron oxide hy-

dioxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.3. When a coating film is produced by using the solvent-based paints, the gloss of the coating film is usually 80 to 115 %, preferably 85 to 115 %; and the heat resistance temperature of the coating film is usually not less than 230°C, preferably not less than 235°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from more than 0 to +100; the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is 30 to 60°. As to the transparency of the coating film, the linear absorption thereof is preferably not more than  $0.05 \mu\text{m}^{-1}$ .

[0134] The water-based paint containing the orange-based fine pigment according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.3. When a coating film is produced by using the water-based paints, the gloss of the coating film is usually 70 to 110 %, preferably 75 to 110 %; and the heat resistance temperature of the coating film is usually not less than 220°C, preferably not less than 225°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10%; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the water-based paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from more than 0 to +100; the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is 30 to 60°. As to the transparency of the coating film, the linear absorption thereof is preferably not more than  $0.05 \mu\text{m}^{-1}$ .

[0135] The water-based paint containing the orange-based fine pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a storage stability ( $\Delta E^*$  value) of usually not more than 1.5, preferably not more than 1.3. When a coating film is produced by using the water-based paints, the gloss of the coating film is usually 75 to 115 %, preferably 80 to 115 %; and the heat resistance temperature of the coating film is usually not less than 230°C, preferably not less than 235°C. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %; and the alkali resistance ( $\Delta G$  value) thereof is usually not more than 12 %, preferably not more than 10 %. As to the hue of the coating film produced from the water-based paint, it is preferred that the  $L^*$  value thereof is 25 to 85; the  $a^*$  value thereof is from more than 0 to +100; the  $b^*$  value thereof is from more than 0 to +100; and the  $h$  value thereof is 30 to 60°. As to the transparency of the coating film, the linear absorption thereof is preferably not more than  $0.05 \mu\text{m}^{-1}$ .

[0136] In the paint of the present invention, the lower limit of the amount of the green or orange-based pigment blended therein usually 0.5 part by weight, preferably 1.0 part by weight, more preferably 2.0 parts by weight based on 100 parts by weight of a paint base material; and the upper limit of the amount of the green or orange-based pigment blended therein is usually 100 parts by weight, preferably 80 parts by weight, more preferably 50 parts by weight based on 100 parts by weight of the paint base material.

[0137] The paint based material contains green or orange-based pigments, resins and solvents, and may optionally contain defoamers, extender pigments, dryers, surfactants, hardeners, auxiliaries and the like, if required.

[0138] As the resins contained in the paint base material, there may be exemplified those ordinarily used for solvent-based paints such as acrylic resins, alkyd resins, polyester resins, polyurethane resins, epoxy resins, phenol resins, melamine resins, amino resins or the like. Also, as the resins for water-based paints, there may be exemplified ordinarily used ones such as water-soluble alkyd resins, water-soluble melamine resins, water-soluble acrylic resins, water-soluble urethane emulsion resins or the like.

[0139] As the solvents for solvent-based paints, there may be exemplified those ordinarily used for solvent-based paints such as toluene, xylene, thinner, butyl acetate, methyl acetate, methyl isobutyl ketone, butyl cellosolve, ethyl cellosolve, butyl alcohol, aliphatic hydrocarbons and mixtures thereof.

[0140] Also, as the solvents for water-based paints, there may be exemplified water, butyl cellosolve, butyl alcohol or the like which are ordinarily used for water-based paints, or mixtures thereof.

[0141] As the defoamer, there may be used commercially available products such as NOPCO 8034 (tradename), SN DEFOAMER 477 (tradename), SN DEFOAMER 5013 (tradename), SN DEFOAMER 247 (tradename) or SN DEFOAMER 382 (tradename) (all produced by SUN NOPCO LTD.); ANTIFOAM 08 (tradename) or EMULGEN 903 (tradename) (both produced by KAO CO., LTD.); or the like.

[0142] Next, the rubber or resin composition colored with the pigment according to the present invention will be described.

(A) Resin composition containing the green-based pigment having an average mayor axial diameter of 0.1 to 1.0  $\mu\text{m}$ :

[0143] The resin composition colored with the green-based pigment according to the present invention has a dis-

persing condition of usually rank 4 or 5, preferably rank 5 when visually observed and evaluated by the method described hereinafter; and a heat resistance temperature of usually not less than 215°C, preferably not less than 220°C. As to the hue of the resin composition, it is preferred that the L\* value thereof is 25 to 85; the a\* value thereof is from -100 to less than 0; and the b\* value thereof is -100 to +100; and the h value thereof is 120 to 240°.

**[0144]** The resin composition colored with the green-based pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a dispersing condition of usually rank 4 or 5, preferably rank 5 when visually observed and evaluated by the method described hereinafter; and a heat resistance temperature of usually not less than 220°C, preferably not less than 225°C. As to the hue of the resin composition, it is preferred that the L\* value thereof is 25 to 85; the a\* value thereof is from -100 to less than 0; the b\* value thereof is -100 to +100; and the h value thereof is 120 to 240°.

(B) Resin composition containing the orange-based pigment having an average major axial diameter of 0.1 to 1.0  $\mu\text{m}$ :

**[0145]** The resin composition colored with the orange-based pigment according to the present invention has a dispersing condition of usually rank 4 or 5, preferably rank 5 when visually observed and evaluated by the method described hereinafter; and a heat resistance temperature of usually not less than 215°C, preferably not less than 220°C. As to the hue of the resin composition, it is preferred that the L\* value thereof is 25 to 85; the a\* value thereof is from more than 0 to +100; the b\* value thereof is from more than 0 to +100; and the h value thereof is 30 to 60°C.

**[0146]** The resin composition colored with the orange-based pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a dispersing condition of usually rank 4 or 5, preferably rank 5 when visually observed and evaluated by the method described hereinafter; and a heat resistance temperature of usually not less than 220°C, preferably not less than 225°C. As to the hue of the resin composition, it is preferred that the L\* value thereof is 25 to 85; the a\* value thereof is from more than 0 to +100; the b\* value thereof is from more than 0 to +100; and the h value thereof is 30 to 60°C.

(C) Resin composition containing the green-based fine pigment having an average major axial diameter of from 0.005  $\mu\text{m}$  to less than 0.1  $\mu\text{m}$ :

**[0147]** The resin composition colored with the green-based fine pigment according to the present invention has a dispersing condition of usually rank 4 or 5, preferably rank 5 when visually observed and evaluated by the method described hereinafter; and a heat resistance temperature of usually not less than 210°C, preferably not less than 215°C. As to the hue of the resin composition, it is preferred that the L\* value thereof is 25 to 85; the a\* value thereof is from -100 to less than 0; the b\* value thereof is -100 to +100; and the h value thereof is 120 to 240°. As to the transparency of the resin composition, the linear absorption thereof is preferably not more than 0.05  $\mu\text{m}^{-1}$ .

**[0148]** The resin composition colored with the green-based fine pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a dispersing condition of usually rank 4 or 5, preferably rank 5 when visually observed and evaluated by the method described hereinafter; and a heat resistance temperature of usually not less than 215°C, preferably not less than 220°C. As to the hue of the resin composition, it is preferred that the L\* value thereof is 25 to 85; the a\* value thereof is from -100 to less than 0; the b\* value thereof is -100 to +100; and the h value thereof is 120 to 240°. As to the transparency of the resin composition, the linear absorption thereof is preferably not more than 0.05  $\mu\text{m}^{-1}$ .

(D) Resin composition containing the orange-based fine pigment having an average major axial diameter of from 0.005 to less than 0.1  $\mu\text{m}$ :

**[0149]** The resin composition colored with the orange-based fine pigment according to the present invention has a dispersing condition of usually rank 4 or 5, preferably rank 5 when visually observed and evaluated by the method described hereinafter; and a heat resistance temperature of usually not less than 210°C, preferably not less than 215°C. As to the hue of the resin composition, it is preferred that the L\* value thereof is 25 to 85; the a\* value thereof is from more than 0 to +100; the b\* value thereof is from more than 0 to +100; and the h value thereof is 30 to 60°. As to the transparency of the resin composition, the linear absorption thereof is preferably not more than 0.05  $\mu\text{m}^{-1}$ .

**[0150]** The resin composition colored with the orange-based fine pigment obtained by using as the core particles iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon according to the present invention, has a dispersing condition of usually rank 4 or 5, preferably rank 5 when visually observed and evaluated by the method described hereinafter; and a heat resistance temperature of usually not less than 215°C, preferably not less than 220°C. As to the hue of the resin composition, it is preferred that the L\* value thereof is 25 to 85; the a\* value thereof is from more than 0 to +100; the b\* value thereof is from more than 0 to +100; and the h value

thereof is 30 to 60°. As to the transparency of the resin composition, the linear absorption thereof is preferably not more than 0.05  $\mu\text{m}^{-1}$ .

[0151] In the resin composition according to the present invention, the amount of the green or orange-based pigment blended is usually 0.01 to 200 parts by weight based on 100 parts by weight of the rubber or resins composition.

In the case where the green or orange-based pigment having a particle size of 0.1 to 1.0  $\mu\text{m}$  is used:

[0152] In the rubber or resin composition of the present invention, the amount of the green or orange-based pigment blended is usually 0.5 to 200 parts by weight based on 100 parts by weight of the rubber or resin composition. In the consideration of good handling property of the resin composition, the amount of the green or orange-based pigment blended is preferably 1.0 to 150 parts by weight, more preferably 2.5 to 100 parts by weight based on 100 parts by weight of the rubber or resin composition.

In the case where the green or orange-based fine pigment having a particle size of from 0.005  $\mu\text{m}$  to less than 0.1  $\mu\text{m}$  is used:

[0153] In the rubber or resin composition according to the present invention, the amount of the green or orange-based fine pigment blended is usually 0.01 to 50 parts by weight based on 100 parts by weight of the rubber or resin composition. In the consideration of good handling property of the resin composition, the amount of the green or orange-based fine pigment blended is preferably 0.05 to 45 parts by weight, more preferably 0.1 to 40 parts by weight based on 100 parts by weight of the rubber or resin composition.

[0154] The based material of the rubber or resin composition according to the present invention contains green or orange-based fine pigments and known thermoplastic resins, and may optionally contain various additives such as lubricants, plasticizers, antioxidants, ultraviolet light absorbers or the like, if required.

[0155] As the rubber or resins of the composition, there may be exemplified natural rubbers, synthetic rubbers, thermoplastic resins (e.g., polyolefins such as polyethylenes, polypropylenes, polybutenes and polyisobutylenes, polyvinyl chlorides, styrene polymers and polyamides) or the like.

[0156] The amount of the additives added is not more than 50 % by weight based on the total weight of the green or orange-based fine pigments and resins. When the amount of the additives added is more than 50 % by weight, the obtained rubber or resin composition is deteriorated in moldability.

[0157] The resin composition according to the present invention may be produced by preliminarily intimately mixing a raw resin material and the green or orange-based fine pigment together and applying a strong shear force to the mixture by a kneader or an extruder to deaggregate agglomerates of the green or orange-based fine pigment and uniformly disperse the individual green or orange-based fine pigment particles in the resin. The thus produced resin composition may be formed into an appropriate shape according to the application thereof upon use.

[0158] Next, the process for producing the green or orange-based pigment according to the present invention, is described.

[0159] The green or orange-based pigment of the present invention can be produced by mixing iron oxide hydroxide particles with alkoxysilane compounds or polysiloxanes to coat the surfaces of the iron oxide hydroxide particles with the alkoxysilane compounds or polysiloxanes; and then mixing the iron oxide hydroxide particles coated with the alkoxysilane compounds or polysiloxanes, with an organic pigment.

[0160] The coating of the iron oxide hydroxide particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes, may be conducted (i) by mechanically mixing and stirring the iron oxide hydroxide particles together with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes; or (ii) by mechanically mixing and stirring both the components together while spraying the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes onto the iron oxide hydroxide particles. In these cases, substantially whole amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes added can be applied onto the surfaces of the iron oxide hydroxide particles.

[0161] In addition, by conducting the above-mentioned mixing or stirring treatment (i) of the iron oxide hydroxide particles as core particles together with the alkoxysilane compounds, at least a part of the alkoxysilane compounds coated on the iron oxide hydroxide particles as core particles may be changed to the organosilane compounds. In this case, there is also no affection against the formation of the organic pigment coat thereon.

[0162] In order to uniformly coat the surfaces of the iron oxide hydroxide particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes, it is preferred that the iron oxide hydroxide particles are preliminarily disaggregated by using a pulverizer.

[0163] As apparatus (a) for mixing and stirring treatment (i) of the core particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes to form the coating layer thereof,



and as apparatus (b) for mixing and stirring treatment (ii) of the organic pigment with the core particles whose surfaces are coated with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes to form the organic pigment coat, there may be preferably used those apparatus capable of applying a shear force to the particles, more preferably those apparatuses capable of conducting the application of shear force, spatulate force and compressed force at the same time.

**[0164]** As such apparatuses, there may be exemplified wheel-type kneaders, ball-type kneaders, blade-type kneaders, roll-type kneaders or the like. Among them, wheel-type kneaders are preferred.

**[0165]** Specific examples of the wheel-type kneaders may include an edge runner (equal to a mix muller, a Simpson mill or a sand mill), a multi-mull, a Stotz mill, a wet pan mill, a Conner mill, a ring muller, or the like. Among them, an edge runner, a multi-mull, a Stotz mill, a wet pan mill and a ring muller are preferred, and an edge runner is more preferred.

**[0166]** Specific examples of the ball-type kneaders may include a vibrating mill or the like. Specific examples of the blade-type kneaders may include a Henschel mixer, a planetary mixer, a Nawter mixer or the like. Specific examples of the roll-type kneaders may include an extruder or the like.

**[0167]** In order to coat the surfaces of the core particles with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes as uniformly as possible, the conditions of the above mixing or stirring treatment may be appropriately controlled such that the linear load is usually 2 to 200 Kg/cm (19.6 to 1960 N/cm), preferably 10 to 150 Kg/cm (98 to 1470 N/cm), more preferably 15 to 100 Kg/cm (147 to 980 N/cm); and the treating time is usually 5 to 120 minutes, preferably 10 to 90 minutes. It is preferred to appropriately adjust the stirring speed in the range of usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm, more preferably 10 to 800 rpm.

**[0168]** The amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes added, is preferably 0.15 to 45 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles. When the amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes or the terminal-modified polysiloxanes added is less than 0.15 part by weight, it may become difficult to adhere the organic pigment in such an amount enough to obtain the iron oxide hydroxide composite particles according to the present invention. On the other hand, when the amount of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes or the terminal-modified polysiloxanes added is more than 45 parts by weight, since a sufficient amount of the organic pigment can be adhered on the surface of the coating layer, it is meaningless to add more than 45 parts by weight.

**[0169]** Next, the organic pigment are added to the iron oxide hydroxide particles coated with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes, and the resultant mixture is mixed and stirred to form the organic pigment coat on the surfaces of the coating layer composed of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes or the terminal-modified polysiloxanes. The drying or heat-treatment may be conducted.

**[0170]** It is preferred that the organic pigment are added little by little and slowly, especially about 5 to 60 minutes.

**[0171]** In order to form organic pigment coat onto the coating layer composed of the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes, or the terminal-modified polysiloxanes as uniformly as possible, the conditions of the above mixing or stirring treatment can be appropriately controlled such that the linear load is usually 2 to 200 Kg/cm (19.6 to 1960 N/cm), preferably 10 to 150 Kg/cm (98 to 1470 N/cm), more preferably 15 to 100 Kg/cm (147 to 980 N/cm); and the treating time is usually 5 to 120 minutes, preferably 10 to 90 minutes. It is preferred to appropriately adjust the stirring speed in the range of usually 2 to 2,000 rpm, preferably 5 to 1,000 rpm, more preferably 10 to 800 rpm.

**[0172]** The preferable amount of the organic blue-based pigment added is 5 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles. When the amount of the organic blue-based pigment added is more than 30 parts by weight, the aimed green-based pigment of the present invention may not be obtained.

**[0173]** The preferable amount of the organic red-based pigment added is 1 to 30 parts by weight based on 100 parts by weight of the iron oxide hydroxide particles. When the amount of the organic red-based pigment added is out of the above specified range, the aimed orange-based pigment of the present invention may not be obtained.

**[0174]** The heating temperature used in the drying and heating steps is usually 40 to 200°C, preferably 60 to 150°C. The treating time of these steps is usually from 10 minutes to 12 hours, preferably from 30 minutes to 3 hours.

**[0175]** When the obtained green or orange-based pigment is subjected to the above drying and heating steps, the alkoxysilane compounds used as the coating thereof are finally converted into organosilane compounds.

**[0176]** If required, prior to mixing and stirring with the alkoxysilane compounds or polysiloxanes, the iron oxide hydroxide particles may be preliminarily coated with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon to form an intermediate coating layer thereon.

**[0177]** At least a part of the surface of the iron oxide hydroxide particles may be coated with at least one compound selected from the group consisting of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon (hereinafter referred to merely as "hydroxides and/or oxides of aluminum and/or silicon"), if required, in ad-



vance of mixing and stirring with the alkoxysilane compounds, the polysiloxanes, the modified polysiloxanes or the terminal-modified polysiloxanes.

**[0178]** The coating of the hydroxides and/or oxides of aluminum and/or silicon may be conducted by adding an aluminum compound, a silicon compound or both the compounds to a water suspension in which the iron oxide hydroxide particles are dispersed, followed by mixing and stirring, and further adjusting the pH value of the suspension, if required, thereby coating the surfaces of the iron oxide hydroxide particles with hydroxides and/or oxides of aluminum and/or silicon. The thus obtained iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon are then filtered out, washed with water, dried and pulverized. Further, the iron oxide hydroxide particles coated with the hydroxides and/or oxides of aluminum and/or silicon may be subjected to posttreatments such as deaeration treatment and compaction treatment, if required.

**[0179]** As the aluminum compounds, there may be exemplified aluminum salts such as aluminum acetate, aluminum sulfate, aluminum chloride or aluminum nitrate, alkali aluminates such as sodium aluminate or the like.

**[0180]** The amount of the aluminum compound added is 0.01 to 20 % by weight (calculated as Al) based on the weight of the iron oxide hydroxide particles. When the amount of the aluminum compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the iron oxide hydroxide particles with hydroxides and/or oxides of aluminum, thereby failing to improve the effective reduction of the organic pigment desorption percentage. On the other hand, when the amount of the aluminum compound added is more than 20 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the aluminum compound.

**[0181]** As the silicon compounds, there may be exemplified #3 water glass, sodium orthosilicate, sodium metasilicate or the like.

**[0182]** The amount of the silicon compound added is 0.01 to 20 % by weight (calculated as  $\text{SiO}_2$ ) based on the weight of the iron oxide hydroxide particles. When the amount of the silicon compound added is less than 0.01 % by weight, it may be difficult to sufficiently coat the surfaces of the iron oxide hydroxide particles with hydroxides and/or oxides of silicon, thereby failing to improve the effective reduction of the organic pigment desorption percentage. On the other hand, when the amount of the silicon compound added is more than 20 % by weight, the coating effect is saturated and, therefore, it is meaningless to add such an excess amount of the silicon compound.

**[0183]** In the case where both the aluminum and silicon compounds are used in combination for the coating, the total amount of the aluminum and silicon compounds added is preferably 0.01 to 20 % by weight (calculated as a sum of Al and  $\text{SiO}_2$ ) based on the weight of the iron oxide hydroxide particles.

**[0184]** The point of the present invention lies in the following. That is, the green or orange-based pigment obtained by coating the surfaces of iron oxide hydroxide particles having an average particle size of 0.1 to 1.0  $\mu\text{m}$  with organosilicon compounds and then adhering an organic blue or red-based pigment onto the surface of coating composed of the organosilicon compounds, is a harmless green or orange-based pigment capable of exhibiting excellent chemical resistances, high hiding power and tinting strength, and improved heat resistance.

**[0185]** Another point of the present invention lies in the following. That is, the green or orange-based fine pigment obtained by coating the surfaces of iron oxide hydroxide particles having an average particle size of from 0.005 to less than 0.1  $\mu\text{m}$  with organosilicon compounds and then adhering an organic blue or red-based pigment onto the surface of coating composed of the organosilicon compounds, is a harmless green or orange-based fine pigment capable of exhibiting excellent chemical resistances, excellent tinting strength and improved heat resistance.

**[0186]** The reason why the pigment exhibiting a green color can be obtained by the present invention, is considered as follows. That is, similarly to such a principle that a film exhibiting a green color is obtained by overlapping a blue film on a yellow film, when the iron oxide hydroxide particles having a yellow color is coated with the organic blue-based pigment having a low hiding power, the obtained composite particles can exhibit a green color.

**[0187]** Also, the reason why the pigment exhibiting an orange color can be obtained by the present invention, is considered as follows. That is, similarly to such a principle that a film exhibiting an orange color is obtained by overlapping a red film on a yellow film, when the iron oxide hydroxide particles having a yellow color is coated with the organic red-based pigment having a low hiding power, the obtained composite particles can exhibit an orange color.

**[0188]** The reason why the green or orange-based pigment of the present invention is excellent in chemical resistances, is considered as follows. That is, the iron oxide hydroxide particles as core particles themselves are excellent in chemical resistances. Further, by selecting the organic blue or red-based pigment to be adhered onto the particles from those pigments having excellent chemical resistances, the obtained green or orange-based pigment can also exhibit excellent chemical resistances as a whole.

**[0189]** The reason why the green or orange-based pigment of the present invention has excellent tinting strength, is considered as follows. That is, the organic blue or red-based pigment is strongly fixed onto the surfaces of the iron oxide hydroxide particles having excellent tinting strength through the coating layer composed of the organosilicon compounds to form composite particles. As a result, the obtained green or orange-based pigment can also exhibit an excellent tinting strength.

**[0190]** The reason why the green or orange-based pigment of the present invention has an excellent heat resistance,

is considered as follows. That is, the iron oxide hydroxide particles which are inherently deteriorated in heat resistance, are coated with the organosilicon compounds having an excellent heat resistance. Further, the organic blue or red-based pigment having an excellent heat resistance is fixed onto the surface of the coating layer composed of the organosilicon compounds. As a result, the obtained green or orange-based pigment can be enhanced in heat resistance.

[0191] The organic green or orange-based pigment according to the present invention contains no harmful elements and compounds and, therefore, can show not only excellent hygiene and safety, but also is effective for environmental protection.

[0192] Also, the green or orange-based pigment having an average major axial diameter of 0.1 to 1.0  $\mu\text{m}$  according to the present invention, has high tinting strength, and excellent heat resistance and chemical resistances, and are harmless.

[0193] In the paint and resin composition of the present invention, there is used the green or orange-based pigment which is not only excellent in heat resistance and chemical resistances but also harmless. Therefore, the paint and resin composition of the present invention is suitable as green or orange paints and resin compositions which are free from environmental pollution.

[0194] The green or orange-based fine pigment having an average major axial diameter of from 0.005 to less than 0.1  $\mu\text{m}$  according to the present invention, is harmless and enhanced in chemical resistances and heat resistance. Further, by using such a green or orange-based fine pigment, it is possible to obtain paints and resin compositions having an excellent transparency. Therefore, the green or orange-based fine pigment of the present invention is suitable as coloring pigments for resins, paints and printing inks.

[0195] The paint and resin composition of the present invention are produced using the green or orange-based fine pigment which has excellent heat resistance and chemical resistances, and is harmless. Therefore, the paint and resin composition of the present invention are suitable as green or orange paints and resin compositions which are free from environmental pollution and have an excellent transparency.

#### EXAMPLES

[0196] The present invention is described in more detail by Examples and Comparative Examples, but the Examples are only illustrative and, therefore, not intended to limit the scope of the present invention.

[0197] Various properties were measured by the following methods.

[0198] (1) The average major axial diameter and average minor axial diameter of the particles were respectively expressed by average values (measured in a predetermined direction) of about 350 particles which were sampled from a micrograph obtained by magnifying an original electron micrograph by four times in each of the longitudinal and transverse directions.

[0199] (2) The aspect ratio of the particles was expressed by a ratio of average major axial diameter to average minor axial diameter thereof.

[0200] (3) The geometrical standard deviation of major axial diameters of the particles was expressed by values obtained by the following method. That is, the major axial diameters were measured from the above magnified electron micrograph. The actual major axial diameters and the number of the particles were obtained from the calculation on the basis of the measured values. On a logarithmic normal probability paper, the major axial diameters were plotted at regular intervals on the abscissa-axis and the accumulative number (under integration sieve) of particles belonging to each interval of the major axial diameters were plotted by percentage on the ordinate-axis by a statistical technique.

[0201] The major axial diameters corresponding to the number of particles of 50 % and 84.13 %, respectively, were read from the graph, and the geometrical standard deviation (under integration sieve) was measured from the following formula:

Geometrical standard deviation =

$$\frac{\{\text{major axial diameter corresponding to 84.13 \% under integration sieve}\} / \{\text{major axial diameter (geometrical average diameter) corresponding to 50 \% under integration sieve}\}}{\quad}$$

[0202] The closer to 1 the geometrical standard deviation value, the more excellent the particle size distribution of

the major axial diameters of the particles.

[0203] (4) The specific surface area was expressed by values measured by a BET method.

[0204] (5) The amounts of Al and Si which were present within iron oxide hydroxide particles or on the surfaces thereof; the amount of Al contained in the aluminum and iron oxide hydroxide composite of adhered onto the surfaces of the iron oxide hydroxide particles; and the amount of Si contained in the coating layer composed of organosilicon compounds, were measured by a fluorescent X-ray spectroscopy device "3063 M-type" (manufactured by RIGAKU DENKI KOGYO CO., LTD.) according to JIS K0119 "General rule of fluorescent X-ray analysis".

[0205] Meanwhile, the amount of Si contained in oxides of silicon, hydroxides of silicon and organosilicon compounds coated on the surfaces of the iron oxide hydroxide particles, is expressed by the value obtained by subtracting the amount of Si measured prior to the respective treatment steps from that measured after the respective treatment steps.

[0206] (6) The amount (wt. %) of Fe contained in aluminum and iron oxide hydroxide composite which was coated on the surfaces of the iron oxide hydroxide particles, is expressed by the value obtained by the following method.

[0207] That is, 0.25 g of the iron oxide hydroxide particles was weighed and charged into a 100 ml conical flask, and then mixed with 33.3 ml of ion exchange water. The flask was placed in a water bath heated to 60°C, and the contents of the flask were stirred for 20 minutes by a magnetic stirrer, thereby obtaining a suspension.

[0208] Next, the suspension was mixed with 16.7 ml of a 12N-hydrochloric acid solution and further stirred for 20 minutes. As a result, a portion of the coat of aluminum and iron oxide hydroxide composite adhered on the surface of each iron oxide hydroxide particle which portion extends from an outer surface of the coat up to approximately a mid point of the distance between the outer surface of the coat and an outer surface of each iron oxide hydroxide particle, and has a substantially uniform composition, was dissolved out with the acid from the outermost surface of the coated particle toward the inside thereof (This fact was already confirmed by many experiments). Thereafter, the suspension containing components dissolved-out by the acid was subjected to suction filtration using a 0.1 µm-membrane filter. The amounts (ppm) of Al and Fe in the obtained filtrate were measured by an inductively-coupled plasma atomic emission spectrometer (SPS-4000 manufactured by Seiko Denshi Kogyo Co., Ltd.).

[0209] Further, the amount of Fe contained in the aluminum and iron oxide hydroxide composite was calculated from the weight percentage of Al to Fe obtained from the measured amounts of Al and Fe in the filtrate and the amount (% by weight) of Al in the aluminum and iron oxide hydroxide composite obtained by the above-mentioned fluorescent X-ray analysis, according to the following formula (i):

$$\text{Amount of Fe (\% by weight)} = \frac{\text{Amount of Al (\% by weight)}}{\text{Weight ratio of Al to Fe}}$$

[0210] (7) The amount of the organic pigment adhered on the iron oxide hydroxide composite particles was obtained by measuring the carbon content thereof using "HORIBA METAL CARBON/SULFUR ANALYZER EMIA-2200 MODEL" (manufactured by Horiba Seisakusho Co., Ltd.).

[0211] (8) The desorption percentage of the organic pigment adhered on the iron oxide hydroxide composite particles, is expressed by the value measured by the following method. The closer to 0% the desorption percentage of the organic pigment, the less the amount of the organic pigment desorbed from the surface of the iron oxide hydroxide composite particles.

[0212] Three grams of the iron oxide hydroxide composite particles and 40 ml of ethanol were placed in a precipitation tube, and subjected to ultrasonic dispersion for 20 minutes. The obtained dispersion was allowed to stand for 120 minutes, thereby separating the dispersion into the iron oxide hydroxide composite particles and the organic pigment desorbed therefrom due to the difference in precipitating speed therebetween. Subsequently, the iron oxide hydroxide composite particles were mixed again with 40 ml of ethanol, and subjected to ultrasonic dispersion for 20 minutes. The obtained dispersion was allowed to stand for 120 minutes, thereby separating the dispersion into the iron oxide hydroxide composite particles and the organic pigment. The thus separated iron oxide hydroxide composite particles were dried at 80°C for one hour to measure the amount of the organic pigment desorbed therefrom. The desorption percentage (%) of the organic pigment is calculated according to the following formula:

Desorption percentage (%) of organic pigment

$$= \{(W_a - W_e) / W_a\} \times 100$$

wherein  $W_a$  represents an amount of the organic pigment adhered onto the iron oxide hydroxide composite particles; and  $W_e$  represents an amount of the organic pigment adhered onto the iron oxide hydroxide composite

particles after desorption test.

[0213] (9) The hue of each of the iron oxide hydroxide particles, the organic pigment and the green or orange-based pigment, were measured by the following method.

[0214] That is, 0.5 g of each sample and 0.5 ml of castor oil were intimately kneaded together by a Hoover's muller to form a paste. 4.5 g of clear lacquer was added to the obtained paste and was intimately mixed to form a paint. The paint was applied on a cast-coated paper by using a 150  $\mu\text{m}$  (6-mil) applicator to produce a coating film piece (having a film thickness of about 30  $\mu\text{m}$ ). The thus obtained coating film piece was measured by a Multi-spectro-colour-meter MSC-IS-2D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.) to determine  $L^*$ ,  $a^*$  and  $b^*$  values thereof.

[0215] Meanwhile, the  $h$  value is expressed by the value calculated from the above measured  $a^*$  and  $b^*$  values according to the following formulae:

$$h = \tan^{-1}(b^*/a^*) \quad (a^* > 0, b^* \leq 0);$$

$$h = 180 + \tan^{-1}(b^*/a^*) \quad (a^* < 0);$$

and

$$h = 360 + \tan^{-1}(b^*/a^*) \quad (a^* > 0, b^* < 0)$$

[0216] (10) The heat resistance of each of the iron oxide hydroxide particles, the organic pigment and the iron oxide hydroxide composite particles, was expressed by the temperature read out from a DSC chart obtained by subjecting a test sample to differential scanning calorimetry (DSC) using a thermal analyzing apparatus SSC-5000 (manufactured by SEIKO DENSHI KOGYO Co., Ltd.), which temperature was read at a crossing point of two tangential lines on two curves constituting the first one of two inflection points which form a peak on the DSC chart.

[0217] (11-1) The tinting strengths of the green-based pigment were measured by the following method.

[0218] That is, a primary color enamel and a vehicle enamel prepared by the following methods were respectively applied on a cast-coated paper by using a 150  $\mu\text{m}$  (6-mil) applicator to produce coating film pieces. The thus obtained coating film pieces were measured by a Multi-spectro-colour-meter MSC-IS-2D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.) to determine the  $L^*$  values thereof. The difference between the measured  $L^*$  values was expressed by  $\Delta L^*$ .

[0219] Based on the thus measured  $\Delta L^*$  value and the  $\Delta L_s^*$  value obtained from chrome green (Comparative Example 6) as a reference sample, the tinting strength (%) was calculated according to the following formula:

$$\text{Tinting strength (\%)} = 100 + \{(\Delta L_s^* - \Delta L^*) \times 10\}$$

[0220] (11-2) The tinting strength of the orange-based pigment was measured by the following method.

[0221] That is, a primary color enamel and a vehicle enamel prepared by the following methods were respectively applied on a cast-coated paper by using a 150  $\mu\text{m}$  (6-mil) applicator to produce coating film pieces. The thus obtained coating film pieces were measured by a Multi-spectro-colour-meter MSC-IS-2D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.) to determine the  $L^*$  values thereof. The difference between the measured  $L^*$  values was expressed by  $\Delta L^*$ .

[0222] Next, the organic red-based pigment and the iron oxide hydroxide particles were simply blended together at the same mixing ratio as used for the production of the orange-based pigment, thereby preparing a mixed pigment as a reference sample for the orange-based pigment. The thus prepared reference sample was used to produce coating film pieces of the primary color enamel and the vehicle enamel by the same method as used above, and then the obtained coating film pieces were measured by the same method as above to determine  $L^*$  values of the respective coating film pieces. The difference between the measured  $L^*$  values was expressed by  $\Delta L_s^*$ .

[0223] Based on the thus obtained  $\Delta L^*$  and  $\Delta L_s^*$  values for the orange-based pigment and the reference sample, respectively, the tinting strength (%) was calculated according to the following formula:

$$\text{Tinting strength (\%)} = 100 + \{(\Delta L_s^* - \Delta L^*) \times 10\}$$

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### Preparation of primary color enamel:

[0224] 10 g of the above sample, 16 g of amino alkyd resin and 6 g of a thinner were blended together. The obtained mixture was charged together with 90 g of 3 mmφ glass beads into a 140-ml glass bottle, and then mixed and dispersed together for 45 minutes using a paint shaker. Thereafter, 50 g of amino alkyd resin was added to the obtained dispersion, and further dispersed together for 5 minutes using a paint shaker, thereby preparing a primary color enamel.

### Preparation of vehicle enamel:

[0225] 12 g of the above-prepared primary color enamel and 40 g of AMIRAC WHITE (titanium dioxide-dispersed amino alkyd resin) were blended together, and then mixed and dispersed together for 15 minutes using a paint shaker, thereby preparing a vehicle enamel.

[0226] (12) The hiding power of the organic pigment and the green or orange-based pigment is expressed by the value measured by the criptometer method according to paragraph 8.2 of JIS K5101, using the above obtained primary color enamel.

[0227] (13) The acid resistance of the iron oxide hydroxide particles and the iron oxide hydroxide composite particles was measured by the following method.

[0228] That is, 10 g of sample particles were immersed in a 5% sulfuric acid solution for 10 minutes. Thereafter, the sample particles were taken out of the sulfuric acid solution, washed with water and then dried. The thus dried particles were used to form a coating film by the same method as described above. The  $L^*$ ,  $a^*$  and  $b^*$  values of the coating film were measured, and the acid resistance was expressed by the value of color difference  $\Delta E^*$  calculated according to the following formula:

$$\Delta E^* \text{ value} = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$$

wherein  $\Delta L^*$  represents the difference between the  $L^*$  values before and after immersing the sample particles in acid or alkali;  $\Delta a^*$  represents the difference between the  $a^*$  values before and after immersing the sample particles in acid or alkali; and  $\Delta b^*$  represents the difference between the  $b^*$  values before and after immersing the sample particles in acid or alkali.

[0229] The smaller the  $\Delta E^*$  value, the more excellent the acid resistance.

[0230] (14) The alkali resistance of the iron oxide hydroxide particles and the iron oxide hydroxide composite particles was measured by the following method.

[0231] That is, 10 g of sample particles were immersed in a 1% sodium hydroxide solution for 15 minutes. Thereafter, the sample particles were taken out of the sodium hydroxide solution, washed with water and then dried. The thus dried particles were used to form a coating film by the same method as described above. The  $L^*$ ,  $a^*$  and  $b^*$  values of the coating film were measured, and the alkali resistance was expressed by the value of color difference  $\Delta E^*$  calculated according to the following formula:

$$\Delta E^* \text{ value} = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$$

wherein  $\Delta L^*$  represents the difference between the  $L^*$  values before and after immersing the sample particles in acid or alkali;  $\Delta a^*$  represents the difference between the  $a^*$  values before and after immersing the sample particles in acid or alkali; and  $\Delta b^*$  represents the difference between the  $b^*$  values before and after immersing the sample particles in acid or alkali.

[0232] The smaller the  $\Delta E^*$  value, the more excellent the alkali resistance.

[0233] (15) The hue of the coating film obtained by using the solvent-based paint or water-based paint containing the green or orange-based pigment was determined by the following method.

[0234] That is, the paint produced by the method described hereinafter, was respectively coated on a cold-rolled steel plate (0.8 mm x 70 mm x 150 mm: JIS G-3141) and then dried to form a coating film having a thickness of 150 μm thereon, thereby preparing a coating film test piece. Also, the hue of the resin composition colored with the green or orange-based pigment was determined using a colored resin plate prepared by the method described hereinafter. The  $L^*$ ,  $a^*$  and  $b^*$  values of the thus prepared coating film test piece and colored resin plate were measured by using a Multi-spectro-colour-meter MSC-IS-2D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.).

[0235] Meanwhile, the h value of the paint or resin composition was calculated from the measured  $a^*$  and  $b^*$  values according to the above-specified formula:

$$h = \tan^{-1}(b^*/a^*) \quad (a^* > 0, b^* \leq 0);$$

$$h = 180 + \tan^{-1}(b^*/a^*) \quad (a^* < 0);$$

and

$$h = 360 + \tan^{-1}(b^*/a^*) \quad (a^* > 0, b^* < 0)$$

[0236] (16) The gloss of a coating film formed obtained by using the paint containing the green or orange-based pigment, was measured by irradiating light onto the above coating film test pieces at an incident angle of 60°, using a glossmeter UGV-5D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.).

[0237] The higher the gloss, the more excellent the dispersibility of the paint containing the green or orange-based pigment.

[0238] (17) The transparency of the solvent-based paint or water-based paint containing the green or orange-based fine pigment, was determined using a coating film having a thickness of 150 µm (6 mil) which was prepared by applying each paint prepared by the method described hereinafter onto a 100 µm-thick clear base film.

[0239] Also, the transparency of the rubber or resin composition was determined using a resin plate prepared by the method described hereinafter.

[0240] In order to determine the transparency of the paint or resin composition, the light transmittance of the coating film or the resin plate was measured by a self-recording photoelectric spectrophotometer "UV-2100" (manufactured by Shimadzu Seisakusho Co., Ltd.). Based on the measured light transmittance, the linear absorption thereof was calculated according to the following formula:

$$\text{Linear absorption } (\mu\text{m}^{-1}) = \ln(1/t)/FT$$

wherein t represents a light transmittance at  $\lambda = 900 \text{ nm}$ ; and FT is a thickness of the coating film or the resin plate used for the measurement.

[0241] The smaller the linear absorption, the higher the light transmittance of the paint or resin composition, i.e., the higher the transparency thereof.

[0242] (18-1) The heat resistance of a coating film formed from the solvent-based paint or water-based paint containing the green or orange-based pigment is determined as follows.

[0243] That is, the above prepared coating film test piece was placed in an electric furnace, and while varying the temperature of the electric furnace, heat-treated for 15 minutes at each temperature. The hues ( $L^*$  value,  $a^*$  value and  $b^*$  value) of the coating film test piece before and after heat treatment at each temperature were respectively measured by a Multi-spectro-colour-meter MSC-IS-2D (manufactured by SUGA TESTING MACHINES MANUFACTURING CO., LTD.).

[0244] Based on the measured values before the heat treatment as standard values, the  $\Delta E^*$  value was calculated according to the below-mentioned formula. On the semi-logarithmic graph paper, the heating temperatures were plotted on the abscissa-axis, and the  $\Delta E^*$  values were plotted on the ordinate-axis. The temperature at which the  $\Delta E^*$  value was identical to just 1.5, was determined as the heat-resisting temperature of the coating film.

$$\Delta E^* \text{ value} = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$$

wherein  $\Delta L^*$  represents a difference between  $L^*$  values of the coating film before and after the heat treatment;  $\Delta a^*$  represents a difference between  $a^*$  values of the coating film before and after the heat treatment; and  $\Delta b^*$  represents a difference between  $b^*$  values of the coating film before and after the heat treatment.

[0245] (18-2) The heat resistance of a coating film formed from the solvent-based paint or water-based paint containing the green or orange-based fine pigment is determined as follows.

[0246] That is, a paint prepared by the method described hereinafter was applied onto a transparent glass plate (0.8 mm (thickness) x 70 mm (width) x 150 mm (length)). The coated glass plate was placed in an electric furnace, and while varying the temperature of the electric furnace, heat-treated for 15 minutes at each temperature. The hues ( $L^*$  value,  $a^*$  value and  $b^*$  value) of the coated glass plate on a standard white back plate before and after heat treatment at each temperature were respectively measured by a Multi-spectro-colour-meter MSC-IS-2D (manufactured by SUGA

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TESTING MACHINES MANUFACTURING CO., LTD.) according to JIS Z 8729.

[0247] Based on the measured values before the heat treatment as standard values, the  $\Delta E^*$  value was calculated according to the above-mentioned formula. On the semi-logarithmic graph paper, the heating temperatures were plotted on the abscissa-axis, and the  $\Delta E^*$  values were plotted on the ordinate-axis. The temperature at which the  $\Delta E^*$  value was identical to just 1.5, was determined as the heat-resisting temperature of the coating film.

$$\Delta E^* \text{ value} = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$$

wherein  $\Delta L^*$  represents a difference between  $L^*$  values of the coating film before and after the heat treatment;  $\Delta a^*$  represents a difference between  $a^*$  values of the coating film before and after the heat treatment; and  $\Delta b^*$  represents a difference between  $b^*$  values of the coating film before and after the heat treatment.

[0248] (19) The heat resistance of a rubber or resin composition containing the green or orange-based pigment was determined as follow. That is, a resin plate prepared by the method described hereinafter was cut into 5 cm square, was placed in a hot press, and while varying the temperature of the hot press and applying a load of 98 MPa (1 ton/cm<sup>2</sup>) thereto, heat-treated for 10 minutes at each temperature. The hues ( $L^*$  value,  $a^*$  value and  $b^*$  value) of the resin plate before and after heat treatment at each temperature were respectively measured. Based on the measured values before the heat treatment as standard values, the  $\Delta E^*$  value was calculated according to the above-mentioned formula. On the semi-logarithmic graph paper, the heating temperatures were plotted on the abscissa-axis, and the  $\Delta E^*$  values were plotted on the ordinate-axis. The temperature at which the  $\Delta E^*$  value was identical to just 1.5, was determined as the heat-resisting temperature of the resin composition.

$$\Delta E^* \text{ value} = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$$

wherein  $\Delta L^*$  represents a difference between  $L^*$  values of the coating film before and after the heat treatment;  $\Delta a^*$  represents a difference between  $a^*$  values of the coating film before and after the heat treatment; and  $\Delta b^*$  represents a difference between  $b^*$  values of the coating film before and after the heat treatment.

[0249] (20-1) The storage stability of a paint containing the green or orange-based pigment was determined by the following method.

[0250] That is, the paint produced by dispersing a mill base prepared by blending the below-mentioned components together at the predetermined mixing ratio, for 90 minutes, was coated on a cold-rolled steel plate (0.8 mm x 70 mm x 150 mm: JIS G-3141) and then dried to form a coating film having a thickness of 150  $\mu$ m thereon. The hue ( $L^*$ ,  $a^*$  and  $b^*$  values) of the thus obtained coating film was measured. Further, after the paint was allowed to stand at 25°C for one week, the paint was applied onto a cold-rolled steel plate and then dried to form a coating film by the same method as described above. Then, the hue ( $L^*$ ,  $a^*$  and  $b^*$  values) of the obtained coating film were also measured. Based on the thus measured  $L^*$ ,  $a^*$  and  $b^*$  values, the  $\Delta E^*$  value was calculated according to the below-mentioned formula:

$$\Delta E^* \text{ value} = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$$

wherein  $\Delta L^*$  represents a difference between  $L^*$  values of the compared coating films prepared from the respective paints before and after the keeping test;  $\Delta a^*$  represents a difference between  $a^*$  values of the compared coating films prepared from the respective paints before and after the keeping test; and  $\Delta b^*$  represents a difference between  $b^*$  values of the compared coating films prepared from the respective paints before and after the keeping test.

[0251] (20-2) The storage stability of a paint containing the green or orange-based fine pigment was determined as follows. That is, the paint prepared by the method described hereinafter, was applied onto a clear base film and then dried to form a coating film having a thickness of 150  $\mu$ m (6 mil) thereon. The  $L^*$ ,  $a^*$  and  $b^*$  values of the obtained coating film were measured. Further, after the paint was allowed to stand at 25°C for one week, the paint was applied onto a clear base film and then dried to form a coating film by the same method as described above. Then, the  $L^*$ ,  $a^*$  and  $b^*$  values of the obtained coating film were also measured. Based on the thus measured  $L^*$ ,  $a^*$  and  $b^*$  values, the  $\Delta E^*$  value was calculated according to the below-mentioned formula:

$$\Delta E^* \text{ value} = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$$

wherein  $\Delta L^*$  represents a difference between  $L^*$  values of the compared coating films prepared from the respective

paints before and after the keeping test;  $\Delta a^*$  represents a difference between  $a^*$  values of the compared coating films prepared from the respective paints before and after the keeping test; and  $\Delta b^*$  represents a difference between  $b^*$  values of the compared coating films prepared from the respective paints before and after the keeping test.

[0252] (21) The acid resistance of a coating film was measured by the following method.

[0253] That is, the coated plate was prepared by the same method as used above for the evaluation of heat resistance. The gloss of the coated plate was measured. Then, the coated plate suspended by a thread was immersed by about 120 mm in depth into a 5 wt. % aqueous sulfuric acid solution filled in a 1,000-ml beaker, and was allowed to stand in the suspended condition at 25°C for 24 hours.

[0254] Next, the coated plate was removed from the aqueous sulfuric acid solution and gently washed with flowing water. After water attached to the coated plate was removed by shaking, the gloss of the coated plate was measured at a central portion thereof. Based on the measured gloss values before and after the immersion, the change in gloss ( $\Delta G$  value) was calculated, thereby evaluating the acid resistance of the coating film. The smaller the  $\Delta G$  value, the more excellent the acid resistance of the coating film.

[0255] (22) The alkali resistance of a coating film was measured by the following method. That is, the coated plate was prepared by the same method as used above for the evaluation of heat resistance. The gloss of the coated plate was measured. Then, the coated plate suspended by a thread was immersed by about 120 mm in depth into a 1 wt. % aqueous sodium hydroxide solution filled in a 1,000-ml beaker, and was allowed to stand in the suspended condition at 25°C for 24 hours.

[0256] Next, the coated plate was removed from the aqueous sodium hydroxide solution and gently washed with flowing water. After water attached to the coated plate was removed by shaking, the gloss of the coated plate was measured at a central portion thereof. Based on the measured gloss values before and after the immersion, the change in gloss ( $\Delta G$  value) was calculated, thereby evaluating the alkali resistance of the coating film. The smaller the  $\Delta G$  value, the more excellent the alkali resistance of the coating film.

[0257] (23) The viscosity at 25°C of the paint prepared by the method described hereinafter, was measured at a shear rate ( $D$ ) of  $1.92 \text{ sec}^{-1}$  by E-type viscometer (cone plate-type viscometer) EMD-R (manufactured by TOKYO KEIKI CO., LTD.).

[0258] (24) The dispersibility of the green or orange-based pigment in resin composition was evaluated by visually counting the number of undispersed aggregate particles on a surface of the colored resin plate produced by the method described hereinafter, and by classifying the results into the following five ranks. The 5th rank represents the most excellent dispersing condition.

Rank 1: not less than 50 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;

Rank 2: 10 to 49 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;

Rank 3: 5 to 9 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;

Rank 4: 1 to 4 undispersed aggregate particles per  $1 \text{ cm}^2$  were recognized;

Rank 5: No undispersed aggregate particles were recognized.

#### Example 1:

##### <Production of green-based pigment>

[0259] 11.0 kg of goethite particles (particle shape: acicular shape; average major axial diameter:  $0.40 \mu\text{m}$ ; aspect ratio: 5.3:1; geometrical standard deviation value: 1.44; BET specific surface area value:  $18.8 \text{ m}^2/\text{g}$ ;  $L^*$  value: 59.3;  $a^*$  value: 16.5;  $b^*$  value: 53.9;  $h$  value:  $73.0^\circ$ ; heat resistance temperature:  $198^\circ\text{C}$ ), were charged into an edge runner "MPUV-2 Model" (tradename, manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.). Then, a methyltriethoxysilane solution prepared by mixing and diluting 220 g of methyltriethoxysilane (tradename: TSL8123, produced by GE Toshiba Silicone Co., Ltd.) with 200 ml of ethanol was added to the goethite particles while operating the edge runner. The resultant mixture was mixed and stirred at a linear load of  $392 \text{ N/cm}$  ( $40 \text{ Kg/cm}$ ) and a stirring speed of 22 rpm for 20 minutes.

[0260] Next, 825 g of an organic blue pigment A (kind: copper phthalocyanine blue; particle shape: granular shape; average major axial diameter:  $0.06 \mu\text{m}$ ; hiding power:  $240 \text{ cm}^2/\text{g}$ ;  $L^*$  value: 17.7;  $a^*$  value: 9.7;  $b^*$  value: -23.4;  $h$  value:  $292.5^\circ$ ; heat resistance temperature:  $256^\circ\text{C}$ ), were added to the above mixture for 10 minutes while operating the edge runner. Further, the obtained mixture was mixed and stirred at a linear load of  $392 \text{ N/cm}$  ( $40 \text{ Kg/cm}$ ) and a stirring speed of 22 rpm for 20 minutes to form a coating layer composed of the organic blue pigment A on the methyltriethoxysilane coat, thereby obtaining a green-based pigment. The obtained green-based pigment was heat-treated at  $105^\circ\text{C}$  for 60 minutes by using a drier.

[0261] The obtained green-based pigment was acicular particles having an average major axial diameter of  $0.40 \mu\text{m}$ , an aspect ratio of 5.3:1, a geometrical standard deviation value of 1.44, a BET specific surface area value of  $20.1$



m<sup>2</sup>/g, a L\* value of 39.9, an a\* value of -13.2, a b\* value of 19.8, a h value of 123.7°, a tinting strength of 141% and a hiding power of 1,950 cm<sup>2</sup>/g. As to the chemical resistances of the green-based pigment, the acid resistance ( $\Delta E^*$  value) thereof was 0.99, and the alkali resistance ( $\Delta E^*$  value) thereof was 0.86. As to the heat resistance of the green-based pigment, the heat resistance temperature thereof was 227°C. The desorption percentage of the organic blue pigment from the green-based pigment was 7.0 % by weight. The amount of a coating layer composed of organosilane compounds produced from methyltriethoxysilane was 0.29 % by weight (calculated as Si). The amount of the coating layer composed of the organic blue pigment A was 4.61 % by weight (calculated as C) (corresponding to 7.5 parts by weight based on 100 parts by weight of the goethite core particles).

[0262] As a result of the observation of electron micrograph, almost no organic blue pigment A liberated was recognized, so that it was confirmed that a substantially whole amount of the organic blue pigment A added was adhered on the coating layer composed of the organosilane compounds produced from methyltriethoxysilane.

#### Example 2:

##### <Production of solvent-based paint containing green-based pigment>

[0263] 10 g of the green-based pigment produced in Example 1, was blended with an amino alkyd resin and a thinner at the following weight ratio, and charged into a 140-ml glass bottle together with 90 g of 3 mm $\phi$  glass beads. Next, the obtained mixture was mixed and dispersed for 90 minutes by a paint shaker, thereby preparing a mill base.

Composition of Mill Base:	
Green-based pigment	12.2 parts by weight
Amino alkyd resin (AMILAC No. 1026, produced by KANSAI PAINT CO., LTD.)	19.5 parts by weight
Thinner	7.3 parts by weight

[0264] The above-prepared mill base was blended with an amino alkyd resin at the following weight ratio, and the obtained mixture was further mixed and dispersed for 15 minutes by a paint shaker, thereby obtaining a solvent-based paint containing the green-based pigment.

Composition of paint:	
Mill base	39.0 parts by weight
Amino alkyd resin (AMILAC No. 1026, produced by KANSAI PAINT CO., LTD.)	61.0 parts by weight

[0265] The thus obtained solvent-based paint showed a viscosity of 1,452 cP. As to the storage stability of the solvent-based paint, the  $\Delta E^*$  value thereof was 0.92.

[0266] Then, the solvent-based paint was applied onto a cold-rolled steel plate (0.8 mm x 70 mm x 150 mm; JIS G-3141) and then dried to form a coating film having a thickness of 150  $\mu$ m thereon. The thus obtained coating film showed a gloss of 87% and a heat resistance temperature of 249°C. As to the hue of the coating film, the L\* value thereof was 40.2; the a\* value thereof was -12.4; the b\* value thereof was 20.5; and the h value thereof was 121.2°. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof was 9.3%, and the alkali resistance ( $\Delta G$  value) thereof was 7.9%.

#### Example 3:

##### <Production of water-based paint containing green-based pigment>

[0267] 7.62 g of the green-based pigment obtained in Example 1, was blended with a water-soluble alkyd resin at the following weight ratio, and charged into a 140-ml glass bottle together with 90 g of 3 mm $\phi$  glass beads. Next, the obtained mixture was mixed and dispersed for 90 minutes by a paint shaker, thereby preparing a mill base.

Composition of Mill Base:	
Green-based pigment	12.4 parts by weight
Water-soluble alkyd resin (tradename: "S-118", produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	9.0 parts by weight
Defoamer (tradename: "NOPCO 8034", produced by SUN NOPCO LTD.)	0.1 parts by weight

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(continued)

Composition of Mill Base:		
5	Water	4.8 parts by weight
	Butyl cellosolve	4.1 parts by weight

[0268] The above-prepared mill base was blended with paint components at the following weight ratio, and the obtained mixture was further mixed and dispersed for 15 minutes by a paint shaker, thereby obtaining a water-soluble paint.

Composition of paint:		
15	Mill base	30.4 parts by weight
	Water-soluble alkyd resin (tradename: S-118, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	46.2 parts by weight
	Water-soluble melamine resin (tradename: S-695, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	12.6 parts by weight
	Defoamer (tradename: "NOPCO 8034", produced by SUN NOPCO LTD.)	0.1 parts by weight
	Water	9.1 parts by weight
20	Butyl cellosolve	1.6 parts by weight

[0269] The thus obtained water-based paint showed a viscosity of 2,118 cP. As to the storage stability of the water-based paint, the  $\Delta E^*$  value thereof was 1.00.

[0270] Then, the water-based paint was applied onto a cold-rolled steel plate (0.8 mm x 70 mm x 150 mm; JIS G-3141) and then dried to form a coating film having a thickness of 150  $\mu$ m thereon. The thus obtained coating film showed a gloss of 82% and a heat resistance temperature of 247°C. As to the hue of the coating film, the  $L^*$  value thereof was 40.7; the  $a^*$  value thereof was -12.6; the  $b^*$  value thereof was 20.9; and the  $h$  value thereof was 121.1°. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof was 9.6%, and the alkali resistance ( $\Delta G$  value) thereof was 8.8%.

## Example 4:

### <Production of resin composition>

[0271] 2.5 g of the green-based pigment obtained in Example 1, and 47.5 g of a polyvinyl chloride resin 103EP8D (produced by NIPPON ZEON CO., LTD.) were weighed and charged into a 100 ml beaker, and intimately mixed together by a spatula, thereby obtaining mixed particles.

[0272] 0.5 g of calcium stearate was added to the mixed particles. The mixed particles were slowly supplied to hot rolls heated to 160°C whose clearance was set to 0.2 mm, and continuously kneaded therebetween until a uniform resin composition was produced. The resin composition kneaded was separated from the hot rolls and used as a raw material for forming a colored resin plate.

[0273] Next, the thus-produced resin composition was interposed between a pair of surface-polished stainless steel plates, placed within a hot press heated to 180°C and subjected to a pressure molding while applying a pressure of 1 ton/cm<sup>2</sup> thereto, thereby obtaining a colored resin plate having a thickness of 1 mm. The thus-produced colored resin plate had a dispersing condition of rank 5 and a heat resistance temperature of 223°C. As to the hue of the resin plate, the  $L^*$  value thereof was 42.2; the  $a^*$  value thereof was -10.8; the  $b^*$  value thereof was 17.9; and the  $h$  value thereof was 121.1°.

## Example 5:

### <Production of orange-based pigment>

[0274] 11.0 kg of goethite particles (particle shape: acicular shape; average major axial diameter: 0.40  $\mu$ m; aspect ratio: 5.3:1; geometrical standard deviation value: 1.44; BET specific surface area value: 18.8 m<sup>2</sup>/g;  $L^*$  value: 59.3;  $a^*$  value: 16.5;  $b^*$  value: 53.9;  $h$  value: 73.0°; heat resistance temperature: 198°C), were charged into an edge runner "MPUV-2 Model" (tradename, manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.). Then, a methyltriethoxysilane solution prepared by mixing and diluting 220 g of methyltriethoxysilane (tradename: TSL8123, produced

by GE Toshiba Silicone Co., Ltd.) with 200 ml of ethanol was added to the goethite particles while operating the edge runner. The resultant mixture was mixed and stirred at a linear load of 392 N/cm (40 Kg/cm) and a stirring speed of 22 rpm for 20 minutes.

[0275] Next, 825 g of an organic red pigment D (kind: quinacridone red; particle shape: granular shape; average major axial diameter: 0.58  $\mu\text{m}$ ; hiding power: 480  $\text{cm}^2/\text{g}$ ; heat resistance temperature: 488°C; L\* value: 37.0; a\* value: 51.9; b\* value: 20.6; h value: 21.6°), were added to the above mixture for 10 minutes while operating the edge runner. Further, the obtained mixture was mixed and stirred at a linear load of 392 N/cm (40 Kg/cm) and a stirring speed of 22 rpm for 20 minutes to form a coating layer composed of the organic red pigment D on the methyltriethoxysilane coat, thereby obtaining an orange-based pigment. The obtained orange-based pigment was heat-treated at 105°C for 60 minutes by using a drier.

[0276] The obtained orange-based pigment was acicular particles having an average major axial diameter of 0.40  $\mu\text{m}$ , an aspect ratio of 5.3:1, a geometrical standard deviation value of 1.44, a BET specific surface area value of 21.2  $\text{m}^2/\text{g}$ , a L\* value of 46.3, an a\* value of 37.1, a b\* value of 42.6, a h value of 48.9°, a tinting strength of 137% and a hiding power of 1,970  $\text{cm}^2/\text{g}$ . As to the chemical resistances of the orange-based pigment, the acid resistance ( $\Delta\text{E}^*$  value) thereof was 0.97, and the alkali resistance ( $\Delta\text{E}^*$  value) thereof was 0.85. As to the heat resistance of the orange-based pigment, the heat resistance temperature thereof was 229°C. The desorption percentage of the organic red pigment from the orange-based pigment was 6.9%. The amount of a coating layer composed of organosilane compounds produced from methyltriethoxysilane was 0.30% by weight (calculated as Si). The amount of the coating layer composed of the organic red pigment D was 5.30 % by weight (calculated as C) (corresponding to 7.5 parts by weight based on 100 parts by weight of the goethite core particles).

[0277] As a result of the observation of electron micrograph, almost no organic red pigment D liberated was recognized, so that it was confirmed that a substantially whole amount of the organic red pigment D added was adhered on the coating layer composed of the organosilane compounds produced from methyltriethoxysilane.

#### Example 6:

##### <Production of solvent-based paint containing orange-based pigment>

[0278] 10 g of the orange-based pigment produced in Example 5, was blended with an amino alkyd resin and a thinner at the following weight ratio, and charged into a 140-ml glass bottle together with 90 g of 3 mm $\phi$  glass beads. Next, the obtained mixture was mixed and dispersed for 90 minutes by a paint shaker, thereby preparing a mill base.

Composition of Mill Base:		
Orange-based pigment		12.2 parts by weight
Amino alkyd resin (AMILAC No. 1026, produced by KANSAI PAINT CO., LTD.)		19.5 parts by weight
Thinner		7.3 parts by weight

[0279] The above-prepared mill base was blended with an amino alkyd resin at the following weight ratio, and the obtained mixture was further mixed and dispersed for 15 minutes by a paint shaker, thereby obtaining a solvent-based paint containing the orange-based pigment.

Composition of paint:		
Mill base		39.0 parts by weight
Amino alkyd resin (AMILAC No. 1026, produced by KANSAI PAINT CO., LTD.)		61.0 parts by weight

[0280] The thus obtained solvent-based paint showed a viscosity of 1,315 cP. As to the storage stability of the solvent-based paint, the  $\Delta\text{E}^*$  value thereof was 0.86.

[0281] Then, the solvent-based paint was applied onto a cold-rolled steel plate (0.8 mm x 70 mm x 150 mm; JIS G-3141) and then dried to form a coating film having a thickness of 150  $\mu\text{m}$  thereon. The thus obtained coating film showed a gloss of 87% and a heat resistance temperature of 250°C. As to the hue of the coating film, the L\* value thereof was 48.0; the a\* value thereof was 36.5; the b\* value thereof was 42.1; and the h value thereof was 49.1°. As to the chemical resistances of the coating film, the acid resistance ( $\Delta\text{G}$  value) thereof was 8.7%, and the alkali resistance ( $\Delta\text{G}$  value) thereof was 7.7%.

Example 7:<Production of water-based paint containing orange-based pigment>

[0282] 7.62 g of the orange-based pigment obtained in Example 5, was blended with a water-soluble alkyd resin and the like at the following weight ratio, and charged into a 140-ml glass bottle together with 90 g of 3 mmφ glass beads. Next, the obtained mixture was mixed and dispersed for 90 minutes by a paint shaker, thereby preparing a mill base.

Composition of Mill Base:		
Orange-based pigment		12.4 parts by weight
Water-soluble alkyd resin (tradename: "S-118", produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)		9.0 parts by weight
Defoamer (tradename: "NOPCO 8034", produced by SUN NOPCO LTD.)		0.1 parts by weight
Water		4.8 parts by weight
Butyl cellosolve		4.1 parts by weight

[0283] The above-prepared mill base was blended with paint components at the following weight ratio, and the obtained mixture was further mixed and dispersed for 15 minutes by a paint shaker, thereby obtaining a water-soluble paint.

Composition of paint:		
Mill base		30.4 parts by weight
Water-soluble alkyd resin (tradename: S-118, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)		46.2 parts by weight
Water-soluble melamine resin (tradename: S-695, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)		12.6 parts by weight
Defoamer (tradename: "NOPCO 8034", produced by SUN NOPCO LTD.)		0.1 parts by weight
Water		9.1 parts by weight
Butyl cellosolve		1.6 parts by weight

[0284] The thus obtained water-based paint showed a viscosity of 2,434 cP. As to the storage stability of the water-based paint, the  $\Delta E^*$  value thereof was 0.98.

[0285] Then, the water-based paint was applied onto a cold-rolled steel plate (0.8 mm x 70 mm x 150 mm; JIS G-3141) and then dried to form a coating film having a thickness of 150  $\mu$ m thereon. The thus obtained coating film showed a gloss of 82% and a heat resistance temperature of 248°C. As to the hue of the coating film, the  $L^*$  value thereof was 48.5; the  $a^*$  value thereof was 36.7; the  $b^*$  value thereof was 42.0; and the  $h$  value thereof was 48.9°. As to the chemical resistances of the coating film, the acid resistance ( $\Delta G$  value) thereof was 9.4%, and the alkali resistance ( $\Delta G$  value) thereof was 8.2%.

Example 8:<Production of resin composition>

[0286] 2.5 g of the orange-based pigment obtained in Example 5, and 47.5 g of a polyvinyl chloride resin 103EP8D (produced by NIPPON ZEON CO., LTD.) were weighed and charged into a 100 ml beaker, and intimately mixed together by a spatula, thereby obtaining mixed particles.

[0287] 0.5 g of calcium stearate was added to the mixed particles. The mixed particles were slowly supplied to hot rolls heated to 160°C whose clearance was set to 0.2 mm, and continuously kneaded therebetween until a uniform resin composition was produced. The resin composition kneaded was separated from the hot rolls and used as a raw material for forming a colored resin plate.

[0288] Next, the thus-produced resin composition was interposed between a pair of surface-polished stainless steel plates, placed within a hot press heated to 180°C and subjected to a pressure molding while applying a pressure of 98 MPa (1 ton/cm<sup>2</sup>) thereto, thereby obtaining a colored resin plate having a thickness of 1 mm. The thus-produced colored resin plate had a dispersing condition of rank 5 and a heat resistance temperature of 224°C. As to the hue of the resin plate, the  $L^*$  value thereof was 49.4; the  $a^*$  value thereof was 36.2; the  $b^*$  value thereof was 41.9; and the  $h$

value thereof was 49.2°.

#### Example 9:

##### <Production of green-based fine pigment>

[0289] 11.0 kg of goethite fine particles (particle shape: acicular shape; average major axial diameter: 0.0710  $\mu\text{m}$ ; average minor axial diameter: 0.0081  $\mu\text{m}$ ; aspect ratio: 8.8:1; geometrical standard deviation value: 1.38; BET specific surface area value: 159.8  $\text{m}^2/\text{g}$ ; aluminum content: 0.83% by weight; L\* value: 51.6; a\* value: 31.4; b\* value: 61.7; h value: 63.0°; acid resistance ( $\Delta\text{G}$  value): 1.92; alkali resistance ( $\Delta\text{G}$  value): 1.75; hiding power: 152  $\text{cm}^2/\text{g}$ ; heat resistance temperature: 245°C), were charged into an edge runner "MPUV-2 Model" (tradename, manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.). Then, a methyltriethoxysilane solution prepared by mixing and diluting 220 g of methyltriethoxysilane (tradename: TSL8123, produced by GE Toshiba Silicone Co., Ltd.) with 200 ml of ethanol was added to the goethite fine particles while operating the edge runner. The resultant mixture was mixed and stirred at a linear load of 392 N/cm (40 Kg/cm) and a stirring speed of 22 rpm for 20 minutes.

[0290] Next, 1,100 g of an organic blue pigment A (kind: copper phthalocyanine blue; particle shape: granular shape; average major axial diameter: 0.06  $\mu\text{m}$ ; hiding power: 240  $\text{cm}^2/\text{g}$ ; L\* value: 17.7; a\* value: 9.7; b\* value: -23.4; h value: 292.5°; heat resistance temperature: 256°C), were added to the above mixture for 10 minutes while operating the edge runner. Further, the obtained mixture was mixed and stirred at a linear load of 392 N/cm (40 Kg/cm) and a stirring speed of 22 rpm for 20 minutes to form a coating layer composed of the organic blue pigment A on the methyltriethoxysilane coat. Then, the obtained particles were heat-treated at 105°C for 60 minutes by using a dryer, thereby obtaining a green-based fine pigment.

[0291] The obtained green-based fine pigment was acicular particles having an average major axial diameter of 0.0722  $\mu\text{m}$ , an average minor axial diameter of 0.0082  $\mu\text{m}$ , an aspect ratio of 8.8:1, a geometrical standard deviation value of 1.33, a BET specific surface area value of 153.6  $\text{m}^2/\text{g}$ , a L\* value of 31.6, an a\* value of -8.7, a b\* value of 0.3, a h value of 178.0°, a tinting strength of 123% and a hiding power of 159  $\text{cm}^2/\text{g}$ . As to the chemical resistances of the green-based fine pigment, the acid resistance ( $\Delta\text{E}^*$  value) thereof was 1.14, and the alkali resistance ( $\Delta\text{E}^*$  value) thereof was 1.06. As to the heat resistance of the green-based fine pigment, the heat resistance temperature thereof was 257°C. The desorption percentage of the organic blue pigment from the green-based fine pigment was 7.1%. The amount of a coating layer composed of organosilane compounds produced from methyltriethoxysilane was 0.30% by weight (calculated as Si). The amount of the coating layer composed of the organic blue pigment A was 5.99 % by weight (calculated as C) (corresponding to 10 parts by weight based on 100 parts by weight of the goethite core fine particles).

[0292] As a result of the observation of electron micrograph, almost no organic blue pigment A liberated was recognized. Therefore, it was confirmed that a substantially whole amount of the organic blue pigment A added was adhered on the coating layer composed of the organosilane compounds produced from methyltriethoxysilane.

#### Example 10:

##### <Production of solvent-based paint containing green-based fine pigment>

[0293] 5 g of the green-based fine pigment produced in Example 9 was blended with the below-mentioned paint base materials at the following weight ratio in a 250-ml glass bottle. Next, the obtained mixture was mixed and dispersed together with 160 g of 3 mm $\phi$  glass beads for 120 minutes by a paint shaker, thereby preparing a solvent-based paint.

Composition of Solvent-based Paint:	
Green-based fine pigment	9.9 parts by weight
Melamine resin (tradename: SUPER-PEKKAMINE J-820-60, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	19.8 parts by weight
Alkyd resin (tradename: BEKKOSOLE 1307-60EL, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	39.6 parts by weight
Xylene	29.7 parts by weight
Butanol	1.0 part by weight

[0294] The thus obtained solvent-based paint showed a viscosity of 1,676 cP. As to the storage stability of the solvent-based paint, the  $\Delta\text{E}^*$  value thereof was 0.87.

[0295] The solvent-based paint was applied onto a clear base film and then dried to form a coating film having a thickness of 150  $\mu\text{m}$  (6 mil) thereon. The thus obtained coating film showed a gloss of 86.1%. As to the hue of the coating film, the  $L^*$  value thereof was 32.3; the  $a^*$  value thereof was -16.3; the  $b^*$  value thereof was 2.0; and the  $h$  value thereof was 173.0°. The linear absorption of the coating film was 0.0184  $\mu\text{m}^{-1}$ .

[0296] Then, the solvent-based paint was applied onto a transparent glass plate (0.8 mm in thickness x 70 mm in width x 150 mm in length) to form a coating film having a thickness of 150  $\mu\text{m}$  (6 mil) thereon. As to the chemical resistances of the obtained coating film, the acid resistance ( $\Delta G$  value) thereof was 8.2%, and the alkali resistance ( $\Delta G$  value) thereof was 7.7%.

[0297] Then, the heat resistance of the coating film was determined as follows. That is, five coated plates were prepared using the solvent-based paint by the same method as described above. The respective coated plates were placed within Geer ovens heated to 210°C, 230°C, 250°C, 270°C and 290°C, respectively, and heat-treated therein for 15 minutes. Thereafter, the coated plates were removed from the ovens to measure the hue values thereof. Based on the hue values before the heat treatment as standard values, the  $\Delta E^*$  value of each coated plate was measured. From the relationship between the heat-treating temperature and the  $\Delta E^*$  value, it was recognized that the temperature at which the  $\Delta E^*$  value was identical to just 1.5, was 269°C.

#### Example 11:

#### <Production of water-based paint containing green-based fine pigment>

[0298] 5 g of the green-based fine pigment produced in Example 9 was blended with the below-mentioned paint base materials at the following weight ratio in a 250-ml glass bottle. Next, the obtained mixture was mixed and dispersed together with 160 g of 3 mm $\phi$  glass beads for 120 minutes by a paint shaker, thereby preparing a water-based paint.

Composition of Water-based Paint:		
Green-based fine pigment		10.1 parts by weight
Water-soluble melamine resin (tradename: S-695, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)		9.3 parts by weight
Water-soluble alkyd resin (tradename: S-118, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)		40.7 parts by weight
Defoamer (tradename: "NOPCO 8034", produced by SUN NOPCO LTD.)		0.2 part by weight
Water		28.2 parts by weight
Butyl cellosolve		11.5 parts by weight

[0299] The thus obtained water-based paint showed a viscosity of 2,184 cP. As to the storage stability of the water-based paint, the  $\Delta E^*$  value thereof was 0.92.

[0300] The water-based paint was applied onto a clear base film and then dried to form a coating film having a thickness of 150  $\mu\text{m}$  (6 mil) thereon. The thus obtained coating film showed a gloss of 82.3%. As to the hue of the coating film, the  $L^*$  value thereof was 32.9; the  $a^*$  value thereof was -16.2; the  $b^*$  value thereof was 2.1; and the  $h$  value thereof was 172.6°. The linear absorption of the coating film was 0.0199  $\mu\text{m}^{-1}$ .

[0301] Then, the water-based paint was applied onto a transparent glass plate (0.8 mm in thickness x 70 mm in width x 150 mm in length) to form a coating film having a thickness of 150  $\mu\text{m}$  (6 mil) thereon. As to the chemical resistances of the obtained coating film, the acid resistance ( $\Delta G$  value) thereof was 8.7%, and the alkali resistance ( $\Delta G$  value) thereof was 8.0%.

[0302] Then, the heat resistance of the coating film was determined as follows. That is, five coated plates were prepared using the water-based paint by the same method as described above. The respective coated plates were placed within Geer ovens heated to 210°C, 230°C, 250°C, 270°C and 290°C, respectively, and heat-treated therein for 15 minutes. Thereafter, the coated plates were removed from the ovens to measure the hue values thereof. Based on the hue values before the heat treatment as standard values, the  $\Delta E^*$  value of each coated plate was measured. From the relationship between the heat-treating temperature and the  $\Delta E^*$  value, it was recognized that the temperature at which the  $\Delta E^*$  value was identical to just 1.5, was 264°C.

Example 12:<Production of resin composition>

**[0303]** 0.5 g of the green-based fine pigment obtained in Example 9, and 49.5 g of a polyvinyl chloride resin 103EP8D (produced by NIPPON ZEON CO., LTD.) were weighed and charged into a 100 ml beaker, and intimately mixed together by a spatula, thereby obtaining mixed particles.

**[0304]** 1.0 g of calcium stearate was added to the mixed particles. The mixed particles were slowly supplied to hot rolls heated to 160°C whose clearance was set to 0.2 mm, and continuously kneaded therebetween until a uniform resin composition was produced. The resin composition kneaded was separated from the hot rolls and used as a raw material for forming a colored resin plate.

**[0305]** Next, the thus-produced resin composition was interposed between a pair of surface-polished stainless steel plates, placed within a hot press heated to 180°C and subjected to a pressure molding while applying a pressure of 98 MPa (1 ton/cm<sup>2</sup>) thereto, thereby obtaining a colored resin plate having a thickness of 1 mm. As to the hue of the resin plate, the L\* value thereof was 32.4; the a\* value thereof was -12.6; the b\* value thereof was 2.4; and the h value thereof was 169.2°. The thus-produced colored resin plate had a dispersing condition of rank 5 and a linear absorption of 0.0192 μm<sup>-1</sup>.

**[0306]** Then, the heat resistance of the resin composition was determined as follows. That is, five colored resin plates were prepared using the resin composition and cut into 5 cm square to prepare 5 test specimens. The respective test specimens were placed within hot presses heated to 185°C, 200°C, 215°C, 230°C and 245°C, respectively, and heat-treated therein for 10 minutes while applying a pressure of 98 MPa (1 ton/cm<sup>2</sup>) thereto. Thereafter, the resin plates were removed from the presses to measure the hue values thereof. Based on the hue values before the heat treatment as standard values, the ΔE\* value of each resin plate was measured. From the relationship between the heat-treating temperature and the ΔE\* value, it was recognized that the temperature at which the ΔE\* value was identical to just 1.5, was 231°C.

Example 13:<Production of orange-based fine pigment>

**[0307]** 11.0 kg of goethite fine particles (particle shape: acicular shape; average major axial diameter: 0.0710 μm; average minor axial diameter: 0.0081 μm; aspect ratio: 8.8:1; geometrical standard deviation value: 1.38; BET specific surface area value: 159.8 m<sup>2</sup>/g; aluminum content: 0.83% by weight; L\* value: 51.6; a\* value: 31.4; b\* value: 61.7; h value: 63.0°; acid resistance: 1.92; alkali resistance: 1.75; hiding power: 152 cm<sup>2</sup>/g; heat resistance temperature: 245°C), were charged into an edge runner "MPUV-2 Model" (tradename, manufactured by MATSUMOTO CHUZO TEKKOSHO CO., LTD.). Then, a methyltriethoxysilane solution prepared by mixing and diluting 220 g of methyltriethoxysilane (tradename: TSL8123, produced by GE Toshiba Silicone Co., Ltd.) with 200 ml of ethanol was added to the goethite fine particles while operating the edge runner. The resultant mixture was mixed and stirred at a linear load of 441 N/cm (45 Kg/cm) and a stirring speed of 22 rpm for 30 minutes.

**[0308]** Next, 1,100 g of an organic red pigment D (kind: quinacridone red; particle shape: granular shape; average major axial diameter: 0.58 μm; hiding power: 480 cm<sup>2</sup>/g; L\* value: 37.0; a\* value: 51.9; b\* value: 20.6; h value: 21.6°; heat resistance temperature: 488°C), was added to the above mixture for 10 minutes while operating the edge runner. Further, the obtained mixture was mixed and stirred at a linear load of 441 N/cm (45 Kg/cm) and a stirring speed of 22 rpm for 30 minutes to form a coating layer composed of the organic red pigment A on the methyltriethoxysilane coat. Then, the obtained particles were heat-treated at 105°C for 60 minutes by using a dryer, thereby obtaining orange-based fine pigment.

**[0309]** The obtained orange-based fine pigment was acicular particles having an average major axial diameter of 0.0720 μm, an average minor axial diameter of 0.0084 μm, an aspect ratio of 8.6:1, a geometrical standard deviation value of 1.38, a BET specific surface area value of 162.1 m<sup>2</sup>/g, a L\* value of 35.2, an a\* value of 49.8, a b\* value of 40.2, a h value of 38.9°, a tinting strength of 129% and a hiding power of 161 cm<sup>2</sup>/g. As to the chemical resistances of the orange-based fine pigment, the acid resistance (ΔE\* value) thereof was 1.09, and the alkali resistance (ΔE\* value) thereof was 1.04. As to the heat resistance of the orange-based fine pigment, the heat resistance temperature thereof was 254°C. The desorption percentage of the organic red pigment from the orange-based fine pigment was 7.0%. The amount of a coating layer composed of organosilane compounds produced from methyltriethoxysilane was 0.30% by weight (calculated as Si). The amount of the coating layer composed of the organic red pigment D was 6.89 % by weight (calculated as C) (corresponding to 10 parts by weight based on 100 parts by weight of the goethite core fine particles).

**[0310]** As a result of the observation of electron micrograph, almost no organic red pigment D liberated was recog-

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nized. Therefore, it was confirmed that a substantially whole amount of the organic red pigment D added was adhered on the coating layer composed of the organosilane compounds produced from methyltriethoxysilane.

### Example 14:

#### <Production of solvent-based paint containing orange-based fine pigment>

[0311] 5 g of the orange-based fine pigment produced in Example 13 was blended with the below-mentioned paint base materials at the following weight ratio in a 250-ml glass bottle. Next, the obtained mixture was mixed and dispersed together with 160 g of 3 mm $\phi$  glass beads for 120 minutes by a paint shaker, thereby preparing a solvent-based paint.

Composition of Solvent-based Paint:	
Orange-based fine pigment	9.9 parts by weight
Melamine resin (tradename: SUPER-PEKKAMINE J-820-60, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	19.8 parts by weight
Alkyd resin (tradename: BEKKOSOLE 1307-60EL, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	39.6 parts by weight
Xylene	29.7 parts by weight
Butanol	1.0 part by weight

[0312] The thus obtained solvent-based paint showed a viscosity of 3,119 cP. As to the storage stability of the solvent-based paint, the  $\Delta E^*$  value thereof was 0.95.

[0313] The solvent-based paint was applied onto a clear base film and then dried to form a coating film having a thickness of 150  $\mu$ m (6 mil) thereon. The thus obtained coating film showed a gloss of 82.2%. As to the hue of the coating film, the  $L^*$  value thereof was 36.0; the  $a^*$  value thereof was 49.5; the  $b^*$  value thereof was 40.6; and the  $h$  value thereof 39.4°. The linear absorption of the coating film was 0.0202  $\mu$ m<sup>-1</sup>.

[0314] Then, the solvent-based paint was applied onto a transparent glass plate (0.8 mm in thickness x 70 mm in width x 150 mm in length) to form a coating film having a thickness of 150  $\mu$ m (6 mil) thereon. As to the chemical resistances of the obtained coating film, the acid resistance ( $\Delta G$  value) thereof was 8.5%, and the alkali resistance ( $\Delta G$  value) thereof was 8.0%.

[0315] Then, the heat resistance of the coating film was determined as follows. That is, five coated plates were prepared using the solvent-based paint by the same method as described above. The respective coated plates were placed within Geer ovens heated to 210°C, 230°C, 250°C, 270°C and 290°C, respectively, and heat-treated therein for 15 minutes. Thereafter, the coated plates were removed from the ovens to measure the hue values thereof. Based on the hue values before the heat treatment as standard values, the  $\Delta E^*$  value of each coated plate was measured. From the relationship between the heat-treating temperature and the  $\Delta E^*$  value, it was recognized that the temperature at which the  $\Delta E^*$  value was identical to just 1.5, was 259°C.

### Example 15:

#### <Production of water-based paint containing orange-based fine pigment>

[0316] 5 g of the orange-based fine pigment produced in Example 13 was blended with the below-mentioned paint base materials at the following weight ratio in a 250-ml glass bottle. Next, the obtained mixture was mixed and dispersed together with 160 g of 3 mm $\phi$  glass beads for 120 minutes by a paint shaker, thereby preparing a water-based paint.

Composition of Water-based Paint:	
Orange-based fine pigment	10.1 parts by weight
Water-soluble melamine resin (tradename: S-695, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	9.3 parts by weight
Water-soluble alkyd resin (tradename: S-118, produced by DAI-NIPPON INK KAGAKU KOGYO CO., LTD.)	40.7 parts by weight
Defoamer (tradename: "NOPCO 8034", produced by SUN NOPCO LTD.)	0.2 part by weight
Water	28.2 parts by weight
Butyl cellosolve	11.5 parts by weight



[0317] The thus obtained water-based paint showed a viscosity of 3,209 cP. As to the storage stability of the water-based paint, the  $\Delta E^*$  value thereof was 0.92.

[0318] The water-based paint was applied onto a clear base film and then dried to form a coating film having a thickness of 150  $\mu\text{m}$  (6 mil) thereon. The thus obtained coating film showed a gloss of 78.8%. As to the hue of the coating film, the  $L^*$  value thereof was 36.1; the  $a^*$  value thereof was 49.4; the  $b^*$  value thereof was 40.2; and the  $h$  value thereof was 39.1°. The linear absorption of the coating film was 0.0215  $\mu\text{m}^{-1}$ .

[0319] Then, the water-based paint was applied onto a transparent glass plate (0.8 mm in thickness x 70 mm in width x 150 mm in length) to form a coating film having a thickness of 150  $\mu\text{m}$  (6 mil) thereon. As to the chemical resistances of the obtained coating film, the acid resistance ( $\Delta G$  value) thereof was 8.7%, and the alkali resistance ( $\Delta G$  value) thereof was 8.1%.

[0320] Then, the heat resistance of the coating film was determined as follows. That is, five coated plates were prepared using the water-based paint by the same method as described above. The respective coated plates were placed within Geer ovens heated to 210°C, 230°C, 250°C, 270°C and 290°C, respectively, and heat-treated therein for 15 minutes. Thereafter, the coated plates were removed from the ovens to measure the hue values thereof. Based on the hue values before the heat treatment as standard values, the  $\Delta E^*$  value of each coated plate was measured. From the relationship between the heat-treating temperature and the  $\Delta E^*$  value, it was recognized that the temperature at which the  $\Delta E^*$  value was identical to just 1.5, was 256°C.

#### Example 16:

##### <Production of resin composition>

[0321] 0.5 g of the orange-based fine pigment obtained in Example 13, and 49.5 g of a polyvinyl chloride resin 103EP8D (produced by NIPPON ZEON CO., LTD.) were weighed and charged into a 100 ml beaker, and intimately mixed together by a spatula, thereby obtaining mixed particles.

[0322] 1.0 g of calcium stearate was added to the mixed particles. The mixed particles were slowly supplied to hot rolls heated to 160°C whose clearance was set to 0.2 mm, and continuously kneaded therebetween until a uniform resin composition was produced. The resin composition kneaded was separated from the hot rolls and used as a raw material for forming a colored resin plate.

[0323] Next, the thus-produced resin composition was interposed between a pair of surface-polished stainless steel plates, placed within a hot press heated to 180°C and subjected to a pressure molding while applying a pressure of 98 MPa (1 ton/cm<sup>2</sup>) thereto, thereby obtaining a colored resin plate having a thickness of 1 mm. As to the hue of the resin plate, the  $L^*$  value thereof was 36.2; the  $a^*$  value thereof was 49.9; the  $b^*$  value thereof was 40.6; and the  $h$  value thereof was 39.1°. The thus-produced colored resin plate had a dispersing condition of rank 5 and a linear absorption of 0.0211  $\mu\text{m}^{-1}$ .

[0324] Then, the heat resistance of the resin composition was determined as follows. That is, five colored resin plates were prepared from the resin composition and cut into 5 cm square to prepare 5 test specimens. The respective test specimens were placed within hot presses heated to 185°C, 200°C, 215°C, 230°C and 245°C, respectively, and heat-treated therein for 10 minutes while applying a pressure of 98 MPa (1 ton/cm<sup>2</sup>) thereto. Thereafter, the resin plates were removed from the presses to measure the hue values thereof. Based on the hue values before the heat treatment as standard values, the  $\Delta E^*$  value of each resin plate was measured. From the relationship between the heat-treating temperature and the  $\Delta E^*$  value, it was recognized that the temperature at which the  $\Delta E^*$  value was identical to just 1.5, was 229°C.

##### Core particles 1 to 4:

[0325] As core particles, iron oxide hydroxide particles having properties shown in Table 1 were prepared.

##### Core particles 5:

[0326] 20 kg of acicular goethite particles (core particles 1) and 150 liters of water were mixed together, thereby obtaining a slurry containing the acicular goethite particles. The pH value of the obtained re-dispersed slurry containing the acicular goethite particles was adjusted to 10.5 using an aqueous sodium hydroxide solution, and then the concentration of the solid content in the slurry was adjusted to 98 g/liter by adding water thereto. After 150 liters of the slurry was heated to 60°C, 2,722 ml of a 1.0 mol/liter sodium aluminate solution (corresponding to 0.5 % by weight (calculated as Al) based on the weight of the acicular goethite particles) was added to the slurry. After allowing the obtained slurry to stand for 30 minutes, the pH value of the obtained slurry was adjusted to 7.5 by adding acetic acid thereto. Further, after allowing the obtained slurry to stand for 30 minutes, the slurry was subjected to filtration, washing

with water, drying and pulverization, thereby obtaining the acicular goethite particles whose surfaces were coated with hydroxides of aluminum.

[0327] The production condition are shown in Table 2, and various properties of the obtained surface-treated acicular goethite particles are shown in Table 3.

#### Core particles 6 to 8:

[0328] The same procedure as defined above for the production of the core particles 5, was conducted except that the respective iron oxide hydroxide particles (core particles 2 to 4) were used instead of the core particles 1, and kinds and amounts of coating materials to be adhered thereon were changed variously, thereby obtaining surface-coated iron oxide hydroxide particles.

[0329] The production condition are shown in Table 2, and various properties of the obtained surface-treated iron oxide hydroxide particles are shown in Table 3.

#### Core particles 9 to 12:

[0330] As core particles, iron oxide hydroxide fine particles having properties shown in Table 4 were prepared.

#### Core particles 13:

[0331] 20 kg of acicular goethite fine particles (core particles 9) and 150 liters of water were mixed together, thereby obtaining a slurry containing the acicular goethite fine particles. The pH value of the obtained re-dispersed slurry containing the acicular goethite fine particles was adjusted to 10.5 using an aqueous sodium hydroxide solution, and then the concentration of the solid content in the slurry was adjusted to 98 g/liter by adding water thereto. After 150 liters of the slurry was heated to 60°C, 5,444 ml of a 5.0 mol/liter sodium aluminate solution (corresponding to 5 % by weight (calculated as Al) based on the weight of the acicular goethite fine particles) was added to the slurry. After allowing the obtained slurry to stand for 30 minutes, the pH value of the obtained slurry was adjusted to 7.5 by adding acetic acid thereto. Further, after allowing the obtained slurry to stand for 30 minutes, the slurry was subjected to filtration, washing with water, drying and pulverization, thereby obtaining the acicular goethite fine particles whose surfaces were coated with hydroxides of aluminum.

[0332] The production condition are shown in Table 5, and various properties of the obtained surface-treated acicular goethite fine particles are shown in Table 6.

#### Core particles 14 to 16:

[0333] The same procedure as defined above for the production of the core particles 13, was conducted except that the respective iron oxide hydroxide particles (core particles 10 to 12) were used instead to the core particles 9, and kinds and amounts of coating materials to be adhered were changed variously, thereby obtaining surface-coated iron oxide hydroxide fine particles.

[0334] The production condition are shown in Table 5, and various properties of the obtained surface-treated iron oxide hydroxide fine particles are shown in Table 6.

[0335] Meanwhile, in "Kind of coating material" of the "surface-treating step" as described in Tables, "A" represents hydroxides of aluminum, and "S" represents oxides of silicon.

#### Organic blue pigments A to C:

[0336] The organic blue pigments having properties shown in Table 7 were prepared.

#### Organic red pigments D and E:

[0337] The organic red pigments having properties shown in Table 7 were prepared.

#### Examples 17 to 24 and Comparative Examples 1 to 5:

[0338] The same procedure as defined in Example 1 was conducted except that kinds of the core particles, kinds and amounts of alkoxysilane compounds, polysiloxanes or silicon compounds added in the coating step, linear loads and times used for the edge runner treatment in the above coating step, kinds and amounts of organic blue pigments added in the organic blue pigment-adhering step, and linear loads and times used for the edge runner treatment in the

above adhering step, were changed variously, thereby obtaining green-based pigments.

[0339] The production conditions are shown in Table 8, and various properties of the obtained green-based pigments are shown in Table 9.

Comparative Examples 6 to 8:

[0340] In these Comparative Examples, chrome green (Comparative Example 6), chromium oxide (Comparative Example 7) and phthalocyanine green (Comparative Example 8) were used solely. The results are shown in Table 9.

Examples 25 to 32 and Comparative Examples 9 to 16:

[0341] The same procedure as defined in Example 2 was conducted except that kinds of green-based pigments were changed variously, thereby obtaining solvent-based paints.

[0342] Various properties of the obtained solvent-based paints and coating films are shown in Table 10.

Examples 33 to 40 and Comparative Examples 17 to 24:

[0343] The same procedure as defined in Example 3 was conducted except that kinds of green-based pigments were changed variously, thereby obtaining water-based paints.

[0344] Various properties of the obtained water-based paints and coating films are shown in Table 11.

Examples 41 to 48 and Comparative Examples 25 to 32:

[0345] The same procedure as defined in Example 4 was conducted except that kinds of green-based pigments were changed variously, thereby obtaining resin compositions.

[0346] The production conditions and various properties of the obtained resin compositions are shown in Table 12.

Examples 49 to 56 and Comparative Examples 33 to 37:

[0347] The same procedure as defined in Example 5 was conducted except that kinds of the core particles, kinds and amounts of alkoxysilane compounds, polysiloxanes or silicon compounds added in the coating step, linear loads and times used for the edge runner treatment in the above coating step, kinds and amounts of organic red pigments added in the organic red pigment-adhering step, and linear loads and times used for the edge runner treatment in the above adhering step, were changed variously, thereby obtaining orange-based pigments.

[0348] The production conditions are shown in Table 13, and various properties of the obtained orange-based pigments are shown in Table 14.

Examples 57 to 64 and Comparative Examples 38 to 42:

[0349] The same procedure as defined in Example 6 was conducted except that kinds of orange-based pigments were changed variously, thereby obtaining solvent-based paints.

[0350] Various properties of the obtained solvent-based paints and coating films are shown in Table 15.

Examples 65 to 72 and Comparative Examples 43 to 47:

[0351] The same procedure as defined in Example 7 was conducted except that kinds of orange-based pigments were changed variously, thereby obtaining water-based paints.

[0352] Various properties of the obtained water-based paints and coating films are shown in Table 16.

Examples 73 to 80 and Comparative Examples 48 to 52:

[0353] The same procedure as defined in Example 8 was conducted except that kinds of orange-based pigments were changed variously, thereby obtaining resin compositions.

[0354] The production conditions and various properties of the obtained resin compositions are shown in Table 17.

Examples 81 to 88 and Comparative Examples 53 to 57:

[0355] The same procedure as defined in Example 9 was conducted except that kinds of the core particles, kinds

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and amounts of alkoxysilane compounds, polysiloxanes or silicon compounds added in the coating step, linear loads and times used for the edge runner treatment in the above coating step, kinds and amounts of organic blue pigments added in the organic blue pigment-adhering step, and linear loads and times used for the edge runner treatment in the above adhering step, were changed variously, thereby obtaining green-based fine pigments.

[0356] The production conditions are shown in Table 18, and various properties of the obtained green-based fine pigments are shown in Table 19.

### Examples 89 to 96 and Comparative Examples 58 to 62:

[0357] The same procedure as defined in Example 10 was conducted except that kinds of green-based fine pigments were changed variously, thereby obtaining solvent-based paints.

[0358] Various properties of the obtained solvent-based paints and coating films are shown in Table 20.

### Examples 97 to 104 and Comparative Examples 63 to 67:

[0359] The same procedure as defined in Example 11 was conducted except that kinds of green-based fine pigments were changed variously, thereby obtaining water-based paints.

[0360] Various properties of the obtained water-based paints and coating films are shown in Table 21.

### Examples 105 to 112 and Comparative Examples 68 to 72:

[0361] The same procedure as defined in Example 12 was conducted except that kinds of green-based fine pigments were changed variously, thereby obtaining resin compositions.

[0362] The production conditions and various properties of the obtained resin compositions are shown in Table 22.

### Examples 113 to 120 and Comparative Examples 73 to 77:

[0363] The same procedure as defined in Example 13 was conducted except that kinds of the core particles, kinds and amounts of alkoxysilane compounds, polysiloxanes or silicon compounds added in the coating step, linear loads and times used for the edge runner treatment in the above coating step, kinds and amounts of organic red pigments added in the organic red pigment-adhering step, and linear loads and times used for the edge runner treatment in the above adhering step, were changed variously, thereby obtaining orange-based fine pigments.

[0364] The production conditions are shown in Table 23, and various properties of the obtained orange-based fine pigments are shown in Table 24.

### Examples 121 to 128 and Comparative Examples 78 to 82:

[0365] The same procedure as defined in Example 14 was conducted except that kinds of orange-based fine pigments were changed variously, thereby obtaining solvent-based paints.

[0366] Various properties of the obtained solvent-based paints and coating films are shown in Table 25.

### Examples 129 to 136 and Comparative Examples 83 to 87:

[0367] The same procedure as defined in Example 15 was conducted except that kinds of orange-based fine pigments were changed variously, thereby obtaining water-based paints.

[0368] Various properties of the obtained water-based paints and coating films are shown in Table 26.

### Examples 137 to 144 and Comparative Examples 88 to 92:

[0369] The same procedure as defined in Example 16 was conducted except that kinds of orange-based fine pigments were changed variously, thereby obtaining resin compositions.

[0370] The production conditions and various properties of the obtained resin compositions are shown in Table 27.

Table 1

Core particles	Kind of iron oxide hydroxide particles	Properties of iron oxide hydroxide particles	
		Particle shape	Average major axial diameter (μm)
Core particles 1	Goethite	Acicular	0.43
Core particles 2	Goethite	Acicular	0.38
Core particles 3	Goethite	Acicular	0.40
Core particles 4	Lepidocrocite	Rectangular	0.20

Table 1 (continued)

Core particles	Properties of iron oxide hydroxide particles			
	Aspect ratio (-)	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Al content within particles (wt. %)
Core particles 1	5.8:1	1.45	16.8	-
Core particles 2	6.1:1	1.39	22.3	-
Core particles 3	5.6:1	1.41	19.8	2.36
Core particles 4	4.6:1	1.41	71.2	-

Table 1 (continued)

Core particles	Properties of iron oxide hydroxide particles				
	Hue				Heat resistance temperatur e (°C)
	L* value (-)	a* value (-)	b* value (-)	h value (°)	
Core particles 1	61.2	15.3	54.8	74.4	202
Core particles 2	58.6	17.1	52.1	71.8	195
Core particles 3	60.6	14.9	55.0	74.8	250
Core particles 4	54.8	20.4	37.6	61.5	193

Table 2

Core particles	Kind of core particles	Surface-treating step		
		Additives		
		Kind	Calculated as	Amount (wt. %)
Core particles 5	Core particles 1	Sodium aluminate	Al	0.5
Core particles 6	Core particles 2	Water glass #3	SiO <sub>2</sub>	0.2
Core particles 7	Core particles 3	Aluminum sulfate	Al	1.0
Core particles 8	Core particles 4	Aluminum sulfate	Al	0.5
		Water glass #3	SiO <sub>2</sub>	1.5



Table 2 (continued)

Core particles	Surface-treating step		
	Coating material		
	Kind	Calculated as	Amount (wt. %)
Core particles 5	A	Al	0.49
Core particles 6	S	SiO <sub>2</sub>	0.18
Core particles 7	A	Al	0.97
Core particles 8	A	Al	0.48
	S	SiO <sub>2</sub>	1.45

Table 3

Core particles	Properties of surface-treated iron oxide hydroxide particles		
	Particle shape	Average major axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Core particles 5	Acicular	0.43	5.8:1
Core particles 6	Acicular	0.38	6.1:1
Core particles 7	Acicular	0.40	5.6:1
Core particles 8	Rectangular	0.21	4.6:1

Table 3 (continued)

Core particles	Properties of surface-treated iron oxide hydroxide particles		
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Al content within particles (wt. %)
Core particles 5	1.45	17.0	-
Core particles 6	1.40	22.5	-
Core particles 7	1.41	19.5	2.34
Core particles 8	1.42	70.8	-

Table 3 (continued)

Core particles	Properties of surface-treated iron oxide hydroxide particles				
	Hue				Heat resistance temperature (°C)
	L* value (-)	a* value (-)	b* value (-)	h value (°)	
Core particles 5	61.3	15.1	54.7	74.6	221
Core particles 6	58.7	17.2	52.3	71.8	208
Core particles 7	60.4	15.0	55.2	74.8	260
Core particles 8	55.0	20.2	37.5	61.7	208

Table 4

Core particles	Kind of iron oxide hydroxide fine particles	Properties of iron oxide hydroxide fine particles	
		Particle shape	Average major axial diameter ( $\mu\text{m}$ )
Core particles 9	Goethite	Acicular	0.0813
Core particles 10	Goethite	Spindle- shaped	0.0571
Core particles 11	Goethite	Acicular	0.0763
Core particles 12	Lepidocrocite	Rectangular	0.0900

Table 4 (continued)

Core particles	Properties of iron oxide hydroxide fine particles		
	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)	Geometrical standard deviation value (-)
Core particles 9	0.0095	8.6:1	1.41
Core particles 10	0.0093	6.1:1	1.35
Core particles 11	0.0118	6.5:1	1.36
Core particles 12	0.0179	5.0:1	1.40

Table 4 (continued)

Core particles	Properties of iron oxide hydroxide fine particles	
	BET specific surface area value (m <sup>2</sup> /g)	Al content within particles (calculated as Al) (wt. %)
Core particles 9	148.9	-
Core particles 10	192.1	2.56
Core particles 11	149.2	1.87
Core particles 12	100.4	-

Table 4 (continued)

Core particles	Properties of iron oxide hydroxide fine particles	
	Composite oxide hydroxide	
	Coating amount of Al (calculated as Al) (wt. %)	Coating amount of Fe (calculated as Fe) (wt. %)
Core particles 9	-	-
Core particles 10	-	-
Core particles 11	1.31	11.0
Core particles 12	-	-



Table 4 (continued)

Core particles	Properties of iron oxide hydroxide fine particles				
	Hue				Hiding power (cm <sup>2</sup> /g)
	L* value (-)	a* value (-)	b* value (-)	h value (°)	
Core particles 9	50.1	29.4	54.2	61.5	171
Core particles 10	52.6	29.6	57.0	65.6	144
Core particles 11	54.3	27.3	58.9	65.1	158
Core particles 12	48.4	33.6	59.4	60.5	209

Table 4 (continued)

Core particles	Properties of iron oxide hydroxide fine particles		
	Chemical resistances		Heat resistance temperature (°C)
	Acid resistance $\Delta E^*$ value (-)	Alkali resistance $\Delta E^*$ value (-)	
Core particles 9	2.05	1.83	192
Core particles 10	1.96	1.72	246
Core particles 11	1.77	1.67	270
Core particles 12	2.24	2.11	189

Table 5

Core particles	Kind of core particles	Surface-treating step		
		Additives		
		Kind	Calculated as	Amount (wt. %)
Core particles 13	Core particles 9	Sodium aluminate	Al	5.0
Core particles 14	Core particles 10	Water glass #3	SiO <sub>2</sub>	2.0
Core particles 15	Core particles 11	Sodium aluminate	Al	1.0
		Water glass #3	SiO <sub>2</sub>	0.5
Core particles 16	Core particles 12	Aluminum sulfate	Al	2.0

Table 5 (continued)

Core particles	Surface-treating step		
	Coating material		
	Kind	Calculated as	Amount (wt. %)
Core particles 13	A	Al	4.75
Core particles 14	S	SiO <sub>2</sub>	1.96
Core particles 15	A	Al	0.98
	S	SiO <sub>2</sub>	0.49
Core particles 16	A	Al	1.96

Table 6

Core particles	Properties of surface-treated iron oxide hydroxide fine particles		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Core particles 13	0.0816	0.0098	8.3:1
Core particles 14	0.0572	0.0094	6.1:1
Core particles 15	0.0765	0.0120	6.4:1
Core particles 16	0.0901	0.0180	5.0:1

Table 6 (continued)

Core particles	Properties of surface-treated iron oxide hydroxide fine particles		
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Al content* <sup>1</sup> within particles (calculated as Al) (wt. %)
Core particles 13	1.42	154.2	-
Core particles 14	1.35	186.6	2.56
Core particles 15	1.37	152.9	1.87
Core particles 16	1.41	109.1	-

\*<sup>1</sup>: Content within core particles

Table 6 (continued)

Core particles	Properties of surface-treated iron oxide hydroxide fine particles	
	Composite oxide hydroxide	
	Coating amount of Al* <sup>1</sup> (calculated as Al) (wt. %)	Coating amount of Fe* <sup>1</sup> (calculated as Fe) (wt. %)
Core particles 13	-	-
Core particles 14	-	-
Core particles 15	1.13	0.64
Core particles 16	-	-

\*1: Coating amount on core particles

Table 6 (continued)

Core particles	Properties of surface-treated iron oxide hydroxide fine particles				
	Hue				Hiding power (cm <sup>2</sup> /g)
	L* value (-)	a* value (-)	b* value (-)	h value (°)	
Core particles 13	51.1	29.1	54.3	61.8	166
Core particles 14	53.8	29.3	57.6	63.0	140
Core particles 15	55.2	26.1	58.1	65.8	152
Core particles 16	49.3	34.0	60.2	60.5	207



Table 6 (continued)

Core particles	Properties of surface-treated iron oxide hydroxide fine particles		
	Chemical resistances		Heat resistance (°C)
	Acid resistance $\Delta E^*$ value (-)	Alkali resistance $\Delta E^*$ value (-)	
Core particles 13	1.98	1.80	222
Core particles 14	1.92	1.71	253
Core particles 15	1.73	1.65	274
Core particles 16	2.18	2.05	208

Table 7

Organic pigment	Properties of organic pigment
	Kind
Organic blue pigment A	Copper phthalocyanine blue (C. I. Pigment Blue 15:1)
Organic blue pigment B	Copper phthalocyanine blue (C. I. Pigment Blue 15:4)
Organic blue pigment C	Copper phthalocyanine blue (C. I. Pigment Blue 15:2)
Organic red pigment D	Quinacridone red
Organic red pigment E	Quinacridone red

Table 7 (continued)

Organic pigment	Properties of organic pigment		
	Particle shape	Average particle size (μm)	Hiding power (cm <sup>2</sup> /g)
Organic blue pigment A	Granular	0.06	240
Organic blue pigment B	Granular	0.08	272
Organic blue pigment C	Granular	0.10	301
Organic red pigment D	Granular	0.58	480
Organic red pigment E	Granular	0.50	220

Table 7 (continued)

Organic pigment	Properties of organic pigment				
	Hue				Heat resistance temperature (°C)
	L* value (-)	a* value (-)	b* value (-)	h value (°)	
Organic blue pigment A	17.7	9.7	-23.4	292.5	256
Organic blue pigment B	17.3	11.6	-26.5	293.6	273
Organic blue pigment C	16.9	12.1	-28.8	292.8	266
Organic red pigment D	37.0	51.9	20.6	21.6	488
Organic red pigment E	28.3	58.0	20.6	19.5	319

Table 8

Examples and Comparative Examples	Kind of core particles	Production of green-based pigment	
		Coating step with alkoxysilane, polysiloxane or silicon compound	
		Additives	
		Kind	Amount added (part by weight)
Example 17	Core particles 1	Methyl triethoxysilane	2.0
Example 18	Core particles 2	Methyl trimethoxysilane	0.5
Example 19	Core particles 3	Phenyl triethoxysilane	2.0
Example 20	Core particles 4	Methyl hydrogen polysiloxane	1.0
Example 21	Core particles 5	Methyl triethoxysilane	1.0
Example 22	Core particles 6	BYK-080	1.0
Example 23	Core particles 7	Isobutyl trimethoxysilane	2.0
Example 24	Core particles 8	TSF4770	1.5
Comparative Example 1	Core particles 1	-	-
Comparative Example 2	Core particles 1	Methyl triethoxysilane	1.0
Comparative Example 3	Core particles 1	Methyl triethoxysilane	1.0
Comparative Example 4	Core particles 1	Methyl triethoxysilane	0.005
Comparative Example 5	Core particles 1	$\gamma$ -aminopropyl triethoxysilane	1.0

Table 8 (continued)

Examples and Comparative Examples	Production of green-based pigment			
	Coating step with alkoxysilane, polysiloxane or silicon compound			
	Edge runner treatment			Coating amount (calculated as Si) (wt. %)
	Linear load		Time (min.)	
	(N/cm)	(Kg/cm)		
Example 17	392	40	15	0.30
Example 18	294	30	20	0.10
Example 19	392	40	20	0.26
Example 20	588	60	20	0.42
Example 21	490	50	15	0.15
Example 22	441	45	15	0.17
Example 23	392	40	20	0.30
Example 24	294	30	30	0.34
Comparative Example 1	-	-	-	-
Comparative Example 2	392	40	20	0.15
Comparative Example 3	392	40	20	0.15
Comparative Example 4	392	40	20	7 x 10 <sup>-4</sup>
Comparative Example 5	392	40	20	0.13

Table 8 (continued)

Examples and Comparative Examples	Production of green-based pigment	
	Adhesion step with organic blue pigment	
	Organic blue pigment	
	Kind	Amount adhered (part by weight)
Example 17	A	10.0
Example 18	A	7.5
Example 19	A	20.0
Example 20	A	5.0
Example 21	A	7.5
Example 22	B	15.0
Example 23	B	10.0
Example 24	B	25.0
Comparative Example 1	A	10.0
Comparative Example 2	A	1.0
Comparative Example 3	A	35.0
Comparative Example 4	A	10.0
Comparative Example 5	A	10.0

Table 8 (continued)

Examples and Comparative Examples	Production of green-based pigment			
	Adhesion step with organic blue pigment			
	Edge runner treatment			Amount adhered (calculated as C) (wt. %)
	Linear load		Time (min.)	
	(N/cm)	(Kg/cm)		
Example 17	392	40	20	6.03
Example 18	294	30	30	4.61
Example 19	294	30	20	11.07
Example 20	392	40	20	3.14
Example 21	490	50	15	4.62
Example 22	441	45	20	8.65
Example 23	294	30	20	6.04
Example 24	588	60	30	13.30
Comparative Example 1	392	40	20	6.02
Comparative Example 2	392	40	20	0.63
Comparative Example 3	392	40	20	17.26
Comparative Example 4	392	40	20	6.02
Comparative Example 5	392	40	20	6.03



Table 9

Examples and Comparative Examples	Properties of green-based pigment	
	Average major axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Example 17	0.43	5.8:1
Example 18	0.38	6.1:1
Example 19	0.41	5.6:1
Example 20	0.20	4.6:1
Example 21	0.43	5.8:1
Example 22	0.38	6.1:1
Example 23	0.40	5.6:1
Example 24	0.21	4.6:1
Comparative Example 1	0.43	5.8:1
Comparative Example 2	0.43	5.8:1
Comparative Example 3	0.43	5.8:1
Comparative Example 4	0.43	5.8:1
Comparative Example 5	0.43	5.8:1
Comparative Example 6	0.20	-
Comparative Example 7	0.21	-
Comparative Example 8	0.60	-

Table 9 (continued)

Examples and Comparative Examples	Properties of green-based pigment		
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Al content within particles (wt. %)
Example 17	1.45	18.3	-
Example 18	1.39	24.6	-
Example 19	1.41	22.1	1.94
Example 20	1.41	73.6	-
Example 21	1.45	19.1	-
Example 22	1.39	25.9	-
Example 23	1.41	20.2	2.09
Example 24	1.41	76.5	-
Comparative Example 1	-	26.8	-
Comparative Example 2	1.45	17.9	-
Comparative Example 3	-	29.3	-
Comparative Example 4	-	26.3	-
Comparative Example 5	-	25.8	-
Comparative Example 6	1.89	10.5	-
Comparative Example 7	2.32	68.2	-
Comparative Example 8	1.76	2.1	-

Table 9 (continued)

Examples and Comparative Examples	Properties of green-based pigment			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 17	35.5	-16.1	12.4	142.4
Example 18	38.8	-12.6	18.2	124.7
Example 19	28.5	-20.1	0.9	177.4
Example 20	36.1	-16.4	-1.2	184.2
Example 21	38.5	-12.3	18.0	124.3
Example 22	31.5	-19.6	4.7	166.5
Example 23	35.0	-16.6	12.8	142.4
Example 24	27.9	-14.8	-10.3	214.8
Comparative Example 1	30.5	-19.6	7.4	159.3
Comparative Example 2	51.2	5.7	43.5	82.5
Comparative Example 3	21.3	-18.6	-6.3	198.7
Comparative Example 4	30.3	-19.1	7.6	158.3
Comparative Example 5	31.0	-19.8	7.6	159.0
Comparative Example 6	39.5	-20.0	22.1	132.1
Comparative Example 7	11.3	-24.8	25.6	134.1
Comparative Example 8	38.5	-19.1	20.8	132.6

Table 9 (continued)

Examples and Comparative Examples	Properties of green-based pigment			
	Tinting strength (%)	Hiding power (cm <sup>2</sup> /g)	Chemical resistances	
			Acid resistance $\Delta E^*$ value (-)	Alkali resistance $\Delta E^*$ value (-)
Example 17	134	1,920	0.93	0.78
Example 18	140	1,960	1.02	0.89
Example 19	125	1,830	0.83	0.71
Example 20	151	2,030	1.37	1.22
Example 21	143	1,950	0.74	0.61
Example 22	121	1,850	0.66	0.52
Example 23	138	1,970	0.79	0.67
Example 24	126	1,820	0.51	0.45
Comparative Example 1	4	1,730	2.16	2.01
Comparative Example 2	186	1,950	1.88	1.75
Comparative Example 3	7	1,680	0.76	0.68
Comparative Example 4	5	1,730	2.05	1.93
Comparative Example 5	5	1,740	2.04	1.92
Comparative Example 6	100	1,180	2.58	2.13
Comparative Example 7	98	420	1.89	2.15
Comparative Example 8	78	680	1.16	1.88

Table 9 (continued)

Examples and Comparative Examples	Properties of green-based pigment	
	Heat resistance temperature (°C)	Desorption percentage of organic pigment (%)
Example 17	231	7.4
Example 18	225	7.1
Example 19	268	8.8
Example 20	220	6.5
Example 21	249	3.4
Example 22	240	4.3
Example 23	275	3.8
Example 24	246	4.6
Comparative Example 1	203	68.4
Comparative Example 2	206	6.3
Comparative Example 3	234	24.6
Comparative Example 4	204	54.8
Comparative Example 5	205	50.3
Comparative Example 6	211	-
Comparative Example 7	228	-
Comparative Example 8	256	-

Table 10

Examples and Comparative Examples	Production of paint	Properties of paint	
	Kind of green-based pigment	Viscosity (cP)	Storage stability (-)
Example 25	Example 17	1,280	0.76
Example 26	Example 18	1,357	0.91
Example 27	Example 19	1,408	0.85
Example 28	Example 20	1,408	0.98
Example 29	Example 21	1,562	0.64
Example 30	Example 22	1,178	0.58
Example 31	Example 23	1,280	0.45
Example 32	Example 24	1,433	0.51
Comparative Example 9	Comparative Example 1	2,560	2.13
Comparative Example 10	Comparative Example 2	1,408	1.53
Comparative Example 11	Comparative Example 3	3,884	2.56
Comparative Example 12	Comparative Example 4	1,562	2.01
Comparative Example 13	Comparative Example 5	3,072	1.99
Comparative Example 14	Comparative Example 6	2,560	2.71
Comparative Example 15	Comparative Example 7	2,432	2.13
Comparative Example 16	Comparative Example 8	640	1.86

Table 10 (continued)

Examples and Comparative Examples	Properties of coating film			
	60° gloss (%)	Heat- resistance temperature of coating film (°C)	Chemical resistances	
			Acid resistance $\Delta G$ value (%)	Alkali resistance $\Delta G$ value (%)
Example 25	86	253	8.1	7.0
Example 26	88	248	9.3	8.0
Example 27	90	270	7.8	6.6
Example 28	85	244	10.8	10.1
Example 29	91	263	6.5	5.6
Example 30	89	256	5.1	4.2
Example 31	93	276	5.4	4.5
Example 32	94	261	4.6	3.1
Comparative Example 9	68	213	16.8	14.8
Comparative Example 10	83	220	14.8	13.9
Comparative Example 11	56	255	7.7	6.7
Comparative Example 12	68	215	15.9	14.3
Comparative Example 13	71	216	15.5	14.1
Comparative Example 14	73	236	31.6	28.3
Comparative Example 15	69	253	21.8	16.9
Comparative Example 16	51	266	11.6	10.2

Table 10 (continued)

Examples and Comparative Examples	Properties of coating film			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 25	37.1	-16.3	12.5	142.5
Example 26	39.9	-11.3	18.6	121.3
Example 27	29.6	-19.8	1.1	176.8
Example 28	37.4	-16.1	-0.6	182.1
Example 29	39.9	-12.0	17.6	124.3
Example 30	32.6	-19.3	4.9	165.8
Example 31	36.6	-15.6	12.6	141.1
Example 32	28.7	-14.3	-10.0	215.0
Comparative Example 9	31.4	-19.0	7.5	158.5
Comparative Example 10	51.7	5.9	43.9	82.3
Comparative Example 11	22.4	-18.1	-6.1	198.6
Comparative Example 12	31.5	-18.9	7.7	157.8
Comparative Example 13	32.0	-19.1	7.8	157.8
Comparative Example 14	41.0	-19.3	21.6	131.8
Comparative Example 15	12.6	-24.6	25.9	133.5
Comparative Example 16	40.0	-18.3	21.6	130.3



Table 11

Examples and Comparative Examples	Production of water- based paint	Properties of paint	
	Kind of green-based pigment	Viscosity (cP)	Storage stability (-)
Example 33	Example 17	2,048	0.83
Example 34	Example 18	2,176	1.02
Example 35	Example 19	2,560	0.98
Example 36	Example 20	2,253	1.06
Example 37	Example 21	2,432	0.76
Example 38	Example 22	1,920	0.68
Example 39	Example 23	1,896	0.50
Example 40	Example 24	1,997	0.56
Comparative Example 17	Comparative Example 1	2,688	2.69
Comparative Example 18	Comparative Example 2	2,944	1.62
Comparative Example 19	Comparative Example 3	4,813	3.13
Comparative Example 20	Comparative Example 4	3,276	2.56
Comparative Example 21	Comparative Example 5	3,226	2.57
Comparative Example 22	Comparative Example 6	4,044	3.16
Comparative Example 23	Comparative Example 7	5,069	2.32
Comparative Example 24	Comparative Example 8	1,920	2.46

Table 11 (continued)

Examples and Comparative Examples	Properties of coating film			
	60° gloss (%)	Heat- resistance temperature of coating film (°C)	Chemical resistances	
			Acid resistance $\Delta G$ value (%)	Alkali resistance $\Delta G$ value (%)
Example 33	82	251	8.9	7.5
Example 34	83	246	9.7	8.9
Example 35	83	266	8.0	7.1
Example 36	81	238	11.5	10.6
Example 37	85	257	7.3	6.0
Example 38	86	246	6.0	4.9
Example 39	88	271	6.3	5.2
Example 40	87	252	5.2	4.4
Comparative Example 17	61	208	18.0	15.8
Comparative Example 18	78	218	15.7	14.3
Comparative Example 19	50	249	8.9	7.6
Comparative Example 20	62	210	17.1	16.8
Comparative Example 21	66	211	16.3	16.5
Comparative Example 22	68	226	32.2	30.8
Comparative Example 23	63	246	22.6	17.8
Comparative Example 24	53	253	12.7	11.0

Table 11 (continued)

Examples and Comparative Examples	Properties of coating film			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 33	37.6	-16.3	12.6	142.3
Example 34	39.8	-11.8	17.3	124.3
Example 35	29.7	-20.1	1.2	176.6
Example 36	37.1	-16.6	-1.1	183.8
Example 37	40.2	-11.8	17.9	123.4
Example 38	32.3	-19.5	4.4	167.3
Example 39	37.0	-15.2	12.2	141.2
Example 40	28.4	-15.0	-9.6	212.6
Comparative Example 17	31.1	-19.1	7.7	158.0
Comparative Example 18	52.0	5.6	44.1	82.8
Comparative Example 19	22.3	-18.0	-5.8	197.9
Comparative Example 20	31.1	-19.0	7.8	157.7
Comparative Example 21	31.7	-19.4	7.9	157.8
Comparative Example 22	40.6	-19.0	22.8	129.8
Comparative Example 23	12.5	-25.3	27.3	132.8
Comparative Example 24	39.6	-19.6	23.6	129.7

Table 12

Examples and Comparative Examples	Production of resin composition	
	Green-based pigment	
	Kind	Amount (part by weight)
Example 41	Example 17	1.0
Example 42	Example 18	1.0
Example 43	Example 19	1.0
Example 44	Example 20	1.0
Example 45	Example 21	1.0
Example 46	Example 22	1.0
Example 47	Example 23	1.0
Example 48	Example 24	1.0
Comparative Example 25	Comparative Example 1	1.0
Comparative Example 26	Comparative Example 2	1.0
Comparative Example 27	Comparative Example 3	1.0
Comparative Example 28	Comparative Example 4	1.0
Comparative Example 29	Comparative Example 5	1.0
Comparative Example 30	Comparative Example 6	1.0
Comparative Example 31	Comparative Example 7	1.0
Comparative Example 32	Comparative Example 8	1.0

Table 12 (continued)

Examples and Comparative Examples	Production of resin composition	
	Resin	
	Kind	Amount (part by weight)
Example 41	Polyvinyl chloride resin	99.0
Example 42	Polyvinyl chloride resin	99.0
Example 43	Polyvinyl chloride resin	99.0
Example 44	Polyvinyl chloride resin	99.0
Example 45	Polyvinyl chloride resin	99.0
Example 46	Polyvinyl chloride resin	99.0
Example 47	Polyvinyl chloride resin	99.0
Example 48	Polyvinyl chloride resin	99.0
Comparative Example 25	Polyvinyl chloride resin	99.0
Comparative Example 26	Polyvinyl chloride resin	99.0
Comparative Example 27	Polyvinyl chloride resin	99.0
Comparative Example 28	Polyvinyl chloride resin	99.0
Comparative Example 29	Polyvinyl chloride resin	99.0
Comparative Example 30	Polyvinyl chloride resin	99.0
Comparative Example 31	Polyvinyl chloride resin	99.0
Comparative Example 32	Polyvinyl chloride resin	99.0

Table 12 (continued)

Examples and Comparative Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kind	Amount (part by weight)	
Example 41	Calcium stearate	2.0	160
Example 42	Calcium stearate	2.0	160
Example 43	Calcium stearate	2.0	160
Example 44	Calcium stearate	2.0	160
Example 45	Calcium stearate	2.0	160
Example 46	Calcium stearate	2.0	160
Example 47	Calcium stearate	2.0	160
Example 48	Calcium stearate	2.0	160
Comparative Example 25	Calcium stearate	2.0	160
Comparative Example 26	Calcium stearate	2.0	160
Comparative Example 27	Calcium stearate	2.0	160
Comparative Example 28	Calcium stearate	2.0	160
Comparative Example 29	Calcium stearate	2.0	160
Comparative Example 30	Calcium stearate	2.0	160
Comparative Example 31	Calcium stearate	2.0	160
Comparative Example 32	Calcium stearate	2.0	160

Table 12 (continued)

Examples and Comparative Examples	Properties of resin composition	
	Dispersion condition (-)	Heat-resistance temperature of resin composition (°C)
Example 41	5	224
Example 42	5	223
Example 43	5	232
Example 44	4	218
Example 45	5	230
Example 46	5	226
Example 47	5	239
Example 48	5	229
Comparative Example 25	2	190
Comparative Example 26	3	200
Comparative Example 27	2	233
Comparative Example 28	3	192
Comparative Example 29	2	196
Comparative Example 30	3	218
Comparative Example 31	3	210
Comparative Example 32	3	228

Table 12 (continued)

Examples and Comparative Examples	Properties of coating film			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 41	39.8	-14.6	12.9	138.8
Example 42	41.3	-9.8	16.9	120.3
Example 43	31.5	-18.4	1.4	175.6
Example 44	38.5	-15.3	-0.8	183.0
Example 45	41.9	-10.8	18.1	120.8
Example 46	34.0	-17.6	4.7	165.0
Example 47	38.9	-14.4	12.5	139.0
Example 48	30.1	-13.6	-9.0	213.5
Comparative Example 25	32.0	-17.4	8.1	155.0
Comparative Example 26	53.6	7.3	44.6	80.7
Comparative Example 27	23.9	-16.2	-5.2	197.8
Comparative Example 28	32.8	-17.3	8.1	154.9
Comparative Example 29	33.6	-17.5	8.2	154.9
Comparative Example 30	42.4	-17.8	23.0	127.7
Comparative Example 31	13.8	-23.9	27.6	130.9
Comparative Example 32	41.1	-18.6	24.0	127.8



Table 13

Examples and Comparative Examples	Kind of core particles	Production of orange- based pigment	
		Coating step with alkoxysilane, polysiloxane or silicon compound	
		Additives	
		Kind	Amount added (part by weight)
Example 49	Core particles 1	Methyl triethoxysilane	1.0
Example 50	Core particles 2	Methyl trimethoxysilane	3.0
Example 51	Core particles 3	Phenyl triethoxysilane	2.0
Example 52	Core particles 4	Methyl hydrogen polysiloxane	1.0
Example 53	Core particles 5	Methyl triethoxysilane	1.0
Example 54	Core particles 6	BYK-080	2.0
Example 55	Core particles 7	Isobutyl trimethoxysilane	1.0
Example 56	Core particles 8	TSF4770	1.0
Comparative Example 33	Core particles 1	-	-
Comparative Example 34	Core particles 1	Methyl triethoxysilane	1.0
Comparative Example 35	Core particles 1	Methyl triethoxysilane	1.0
Comparative Example 36	Core particles 1	Methyl triethoxysilane	0.005
Comparative Example 37	Core particles 1	$\gamma$ -aminopropyl triethoxysilane	1.0

Table 13 (continued)

Examples and Comparative Examples	Production of orange-based pigment			
	Coating step with alkoxysilane, polysiloxane or silicon compound			
	Edge runner treatment			Coating amount (calculated as Si) (wt. %)
	Linear load		Time (min.)	
	(N/cm)	(Kg/cm)		
Example 49	588	60	20	0.15
Example 50	294	30	30	0.59
Example 51	441	45	30	0.27
Example 52	588	60	20	0.44
Example 53	294	30	30	0.15
Example 54	392	40	30	0.36
Example 55	588	60	30	0.15
Example 56	392	40	20	0.34
Comparative Example 33	-	-	-	-
Comparative Example 34	392	40	20	0.15
Comparative Example 35	392	40	20	0.15
Comparative Example 36	392	40	20	7 x 10 <sup>-4</sup>
Comparative Example 37	392	40	20	0.13

Table 13 (continued)

Examples and Comparative Examples	Production of orange-based pigment	
	Adhesion step with organic red pigment	
	Organic red pigment	
	Kind	Amount adhered (part by weight)
Example 49	D	10.0
Example 50	E	20.0
Example 51	D	15.0
Example 52	E	20.0
Example 53	D	10.0
Example 54	E	7.5
Example 55	D	10.0
Example 56	E	20.0
Comparative Example 33	D	10.0
Comparative Example 34	D	100.0
Comparative Example 35	D	0.5
Comparative Example 36	D	10.0
Comparative Example 37	D	10.0

Table 13 (continued)

Examples and Comparative Examples	Production of orange-based pigment			
	Adhesion step with organic red pigment			
	Edge runner treatment			Amount adhered (calculated as C) (wt. %)
	Linear load		Time (min.)	
	(N/cm)	(Kg/cm)		
Example 49	392	40		
Example 50	588	60	20	12.78
Example 51	294	30	30	9.99
Example 52	588	60	20	12.80
Example 53	441	45	30	6.96
Example 54	392	40	30	5.33
Example 55	588	60	20	6.93
Example 56	588	60	20	12.77
Comparative Example 33	392	40	20	6.92
Comparative Example 34	392	40	20	38.26
Comparative Example 35	392	40	20	0.35
Comparative Example 36	392	40	20	6.95
Comparative Example 37	392	40	20	6.94

Table 14

Examples and Comparative Examples	Properties of orange-based pigment	
	Average major axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Example 49	0.43	5.8:1
Example 50	0.39	6.1:1
Example 51	0.40	5.6:1
Example 52	0.20	4.6:1
Example 53	0.43	5.8:1
Example 54	0.38	6.1:1
Example 55	0.40	5.6:1
Example 56	0.21	4.6:1
Comparative Example 33	0.43	5.8:1
Comparative Example 34	0.43	5.8:1
Comparative Example 35	0.43	5.8:1
Comparative Example 36	0.43	5.8:1
Comparative Example 37	0.43	5.8:1

Table 14 (continued)

Examples and Comparative Examples	Properties of orange-based pigment		
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Al content within particles (wt. %)
Example 49	1.45	21.3	-
Example 50	1.39	23.2	-
Example 51	1.41	21.6	2.00
Example 52	1.41	71.6	-
Example 53	1.45	21.8	-
Example 54	1.39	24.5	-
Example 55	1.41	23.8	2.09
Example 56	1.42	72.6	-
Comparative Example 33	-	28.6	-
Comparative Example 34	-	34.0	-
Comparative Example 35	1.45	16.3	-
Comparative Example 36	-	26.8	-
Comparative Example 37	-	24.6	-

Table 14 (continued)

Examples and Comparative Examples	Properties of orange-based pigment			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 49	45.7	38.3	38.6	45.2
Example 50	39.3	47.2	35.6	37.0
Example 51	40.3	46.2	38.3	39.7
Example 52	36.2	50.9	34.2	33.9
Example 53	46.1	39.6	36.6	42.7
Example 54	47.5	36.2	43.8	50.4
Example 55	42.8	38.4	41.1	46.9
Example 56	37.7	50.5	33.3	33.4
Comparative Example 33	46.3	37.6	40.4	47.1
Comparative Example 34	31.2	51.2	27.0	27.8
Comparative Example 35	52.8	20.1	45.5	66.2
Comparative Example 36	46.9	38.2	39.2	45.7
Comparative Example 37	47.3	37.9	40.1	46.6

Table 14 (continued)

Examples and Comparative Examples	Properties of orange-based pigment			
	Tinting strength (%)	Hiding power (cm <sup>2</sup> /g)	Chemical resistances	
			Acid resistance	Alkali resistance
			$\Delta E^*$ value (-)	$\Delta E^*$ value (-)
Example 49	136	1,990	1.09	0.91
Example 50	138	1,950	0.94	0.85
Example 51	141	1,940	0.99	0.89
Example 52	145	1,920	1.20	1.19
Example 53	143	2,000	0.88	0.78
Example 54	138	2,070	0.90	0.80
Example 55	146	2,010	0.83	0.72
Example 56	143	1,960	0.97	0.90
Comparative Example 33	100	1,730	2.32	2.10
Comparative Example 34	112	2,010	1.65	1.38
Comparative Example 35	105	1,930	2.09	1.66
Comparative Example 36	102	1,740	2.11	1.95
Comparative Example 37	103	1,780	2.10	1.93



Table 14 (continued)

Examples and Comparative Examples	Properties of orange-based pigment	
	Heat resistance temperature (°C)	Desorption percentage of organic pigment (%)
Example 49	233	7.2
Example 50	235	9.3
Example 51	270	8.6
Example 52	231	9.0
Example 53	250	4.3
Example 54	236	2.1
Example 55	279	3.8
Example 56	239	4.6
Comparative Example 33	205	69.2
Comparative Example 34	241	59.4
Comparative Example 35	203	-
Comparative Example 36	205	58.1
Comparative Example 37	206	56.6

Table 15

Examples and Comparative Examples	Production of paint	Properties of paint	
	Kind of orange-based pigment	Viscosity (cP)	Storage stability $\Delta E^*$ value (-)
Example 57	Example 49	1,280	0.81
Example 58	Example 50	1,196	0.92
Example 59	Example 51	982	0.88
Example 60	Example 52	1,442	0.90
Example 61	Example 53	1,386	0.60
Example 62	Example 54	1,272	0.49
Example 63	Example 55	1,071	0.55
Example 64	Example 56	1,121	0.65
Comparative Example 38	Comparative Example 33	2,560	2.16
Comparative Example 39	Comparative Example 34	2,883	2.93
Comparative Example 40	Comparative Example 35	982	1.62
Comparative Example 41	Comparative Example 36	3,160	2.09
Comparative Example 42	Comparative Example 37	2,830	2.06

Table 15 (continued)

Examples and Comparative Examples	Properties of coating film			
	60° gloss (%)	Heat- resistance temperature of coating film (°C)	Chemical resistances	
			Acid resistance $\Delta G$ value (%)	Alkali resistance $\Delta G$ value (%)
Example 57	87	250	8.3	7.1
Example 58	86	252	7.8	6.9
Example 59	89	271	8.1	7.1
Example 60	85	248	10.4	10.0
Example 61	92	262	6.5	5.2
Example 62	93	253	6.6	5.4
Example 63	95	282	5.9	4.3
Example 64	90	257	7.7	7.0
Comparative Example 38	66	214	16.3	14.9
Comparative Example 39	53	256	14.2	13.3
Comparative Example 40	77	211	15.6	14.0
Comparative Example 41	67	213	16.0	14.9
Comparative Example 42	69	215	15.8	14.5

Table 15 (continued)

Examples and Comparative Examples	Properties of coating film			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 57	47.6	37.6	38.4	45.6
Example 58	41.7	46.6	35.1	37.0
Example 59	42.3	46.9	38.0	39.0
Example 60	37.4	49.1	34.6	35.2
Example 61	48.1	40.3	36.2	41.9
Example 62	49.2	35.5	44.6	51.5
Example 63	43.6	39.2	40.9	46.2
Example 64	49.3	49.8	33.0	33.5
Comparative Example 38	47.5	37.0	40.2	47.4
Comparative Example 39	41.2	51.1	26.8	27.7
Comparative Example 40	54.6	20.6	45.7	65.7
Comparative Example 41	48.9	39.3	39.9	45.4
Comparative Example 42	48.4	36.6	40.4	47.8

Table 16

Examples and Comparative Examples	Production of water- based paint	Properties of paint	
	Kind of orange-based pigment	Viscosity (cP)	Storage stability $\Delta E^*$ value (-)
Example 65	Example 49	2,560	0.92
Example 66	Example 50	2,283	1.01
Example 67	Example 51	2,762	0.96
Example 68	Example 52	2,836	1.00
Example 69	Example 53	2,401	0.71
Example 70	Example 54	2,320	0.59
Example 71	Example 55	2,532	0.64
Example 72	Example 56	2,689	0.77
Comparative Example 43	Comparative Example 33	3,882	2.62
Comparative Example 44	Comparative Example 34	4,156	3.36
Comparative Example 45	Comparative Example 35	2,160	1.74
Comparative Example 46	Comparative Example 36	4,442	2.47
Comparative Example 47	Comparative Example 37	3,716	2.43

Table 16 (continued)

Examples and Comparative Examples	Properties of coating film			
	60° gloss (%)	Heat- resistance temperature of coating film (°C)	Chemical resistances	
			Acid resistance $\Delta G$ value (%)	Alkali resistance $\Delta G$ value (%)
Example 65	84	246	8.9	8.2
Example 66	81	251	8.2	7.6
Example 67	85	268	8.6	7.8
Example 68	81	245	10.9	10.5
Example 69	87	259	6.8	5.7
Example 70	89	250	7.0	5.9
Example 71	90	280	6.3	5.0
Example 72	85	254	8.1	7.7
Comparative Example 43	60	211	17.5	15.6
Comparative Example 44	47	252	15.5	15.0
Comparative Example 45	71	207	16.4	14.8
Comparative Example 46	62	210	16.8	15.6
Comparative Example 47	63	212	17.2	15.3

Table 16 (continued)

Examples and Comparative Examples	Properties of coating film			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 65	47.7	37.5	38.0	45.4
Example 66	41.9	46.8	35.4	37.1
Example 67	42.0	46.6	38.3	39.4
Example 68	37.6	49.2	34.5	35.0
Example 69	47.8	40.6	36.0	41.6
Example 70	49.1	35.7	44.8	51.4
Example 71	43.3	39.5	41.1	46.1
Example 72	49.0	50.0	32.9	33.3
Comparative Example 43	47.2	37.3	40.3	47.2
Comparative Example 44	41.6	51.4	26.5	27.3
Comparative Example 45	55.0	20.9	45.8	65.5
Comparative Example 46	48.3	39.1	39.7	45.4
Comparative Example 47	48.1	36.8	40.2	47.5

Table 17

Examples and Comparative Examples	Production of resin composition	
	Orange-based pigment	
	Kind	Amount (part by weight)
Example 73	Example 49	1.0
Example 74	Example 50	1.0
Example 75	Example 51	1.0
Example 76	Example 52	1.0
Example 77	Example 53	1.0
Example 78	Example 54	1.0
Example 79	Example 55	1.0
Example 80	Example 56	1.0
Comparative Example 48	Comparative Example 33	1.0
Comparative Example 49	Comparative Example 34	1.0
Comparative Example 50	Comparative Example 35	1.0
Comparative Example 51	Comparative Example 36	1.0
Comparative Example 52	Comparative Example 37	1.0



Table 17 (continued)

Examples and Comparative Examples	Production of resin composition	
	Resin	
	Kind	Amount (part by weight)
Example 73	Polyvinyl chloride resin	99.0
Example 74	Polyvinyl chloride resin	99.0
Example 75	Polyvinyl chloride resin	99.0
Example 76	Polyvinyl chloride resin	99.0
Example 77	Polyvinyl chloride resin	99.0
Example 78	Polyvinyl chloride resin	99.0
Example 79	Polyvinyl chloride resin	99.0
Example 80	Polyvinyl chloride resin	99.0
Comparative Example 48	Polyvinyl chloride resin	99.0
Comparative Example 49	Polyvinyl chloride resin	99.0
Comparative Example 50	Polyvinyl chloride resin	99.0
Comparative Example 51	Polyvinyl chloride resin	99.0
Comparative Example 52	Polyvinyl chloride resin	99.0

Table 17 (continued)

Examples and Comparative Examples	Production of resin composition		
	Additives		Kneading temperature (°C)
	Kind	Amount (part by weight)	
Example 73	Calcium stearate	2.0	160
Example 74	Calcium stearate	2.0	160
Example 75	Calcium stearate	2.0	160
Example 76	Calcium stearate	2.0	160
Example 77	Calcium stearate	2.0	160
Example 78	Calcium stearate	2.0	160
Example 79	Calcium stearate	2.0	160
Example 80	Calcium stearate	2.0	160
Comparative Example 48	Calcium stearate	2.0	160
Comparative Example 49	Calcium stearate	2.0	160
Comparative Example 50	Calcium stearate	2.0	160
Comparative Example 51	Calcium stearate	2.0	160
Comparative Example 52	Calcium stearate	2.0	160

Table 17 (continued)

Examples and Comparative Examples	Properties of resin composition	
	Dispersion condition (-)	Heat-resistance temperature of resin composition (°C)
Example 73	5	226
Example 74	5	229
Example 75	5	232
Example 76	5	223
Example 77	5	231
Example 78	5	226
Example 79	5	238
Example 80	5	230
Comparative Example 48	2	192
Comparative Example 49	2	224
Comparative Example 50	3	193
Comparative Example 51	2	195
Comparative Example 52	2	196

Table 17 (continued)

Examples and Comparative Examples	Properties of resin composition			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 73	49.7	36.3	38.3	46.5
Example 74	43.8	45.3	35.0	37.7
Example 75	43.9	44.9	38.1	40.3
Example 76	39.5	47.8	34.7	36.0
Example 77	49.6	38.6	35.9	42.9
Example 78	51.0	34.1	44.5	52.5
Example 79	45.1	38.2	41.3	47.2
Example 80	50.7	48.2	32.8	34.2
Comparative Example 48	49.2	35.6	40.0	48.3
Comparative Example 49	43.3	50.0	26.1	27.6
Comparative Example 50	56.4	19.4	45.4	66.9
Comparative Example 51	50.0	37.3	39.9	46.9
Comparative Example 52	49.9	34.9	40.2	49.0

Table 18

Examples and Comparative Examples	Kind of core particles	Production of green-based fine pigment	
		Coating step with alkoxysilane, polysiloxane or silicon compound	
		Additives	
		Kind	Amount added (part by weight)
Example 81	Core particles 9	Methyl triethoxysilane	1.0
Example 82	Core particles 10	Methyl trimethoxysilane	0.5
Example 83	Core particles 11	Phenyl triethoxysilane	2.0
Example 84	Core particles 12	Methyl hydrogen polysiloxane	1.0
Example 85	Core particles 13	Methyl triethoxysilane	2.0
Example 86	Core particles 14	Methyl triethoxysilane	1.0
Example 87	Core particles 15	Methyl triethoxysilane	1.5
Example 88	Core particles 16	Methyl triethoxysilane	3.0
Comparative Example 53	Core particles 9	-	-
Comparative Example 54	Core particles 9	Methyl triethoxysilane	1.0
Comparative Example 55	Core particles 9	Methyl triethoxysilane	0.005
Comparative Example 56	Core particles 9	Methyl triethoxysilane	1.0
Comparative Example 57	Core particles 9	$\gamma$ -aminopropyl triethoxysilane	1.0

Table 18 (continued)

Examples and Comparative Examples	Production of green-based fine pigment			
	Coating step with alkoxysilane, polysiloxane or silicon compound			
	Edge runner treatment			Coating amount (calculated as Si) (wt. %)
	Linear load		Time (min.)	
	(N/cm)	(Kg/cm)		
Example 81	392	40	30	0.15
Example 82	588	60	20	0.10
Example 83	490	50	20	0.26
Example 84	294	30	30	0.42
Example 85	588	60	20	0.30
Example 86	441	45	20	0.15
Example 87	735	75	20	0.23
Example 88	441	45	30	0.45
Comparative Example 53	-	-	-	-
Comparative Example 54	588	60	20	0.15
Comparative Example 55	588	60	20	6 x 10 <sup>-4</sup>
Comparative Example 56	588	60	20	0.15
Comparative Example 57	588	60	20	0.12

Table 18 (continued)

Examples and Comparative Examples	Production of green-based fine pigment	
	Adhesion step with organic blue pigment	
	Organic blue pigment	
	Kind	Amount adhered (part by weight)
Example 81	A	10.0
Example 82	B	7.5
Example 83	C	15.0
Example 84	A	20.0
Example 85	A	15.0
Example 86	A	12.0
Example 87	A	7.5
Example 88	A	10.0
Comparative Example 53	A	10.0
Comparative Example 54	-	-
Comparative Example 55	A	10.0
Comparative Example 56	A	1.0
Comparative Example 57	A	10.0

Table 18 (continued)

Examples and Comparative Examples	Production of green-based fine pigment			
	Adhesion step.with organic blue pigment			
	Edge runner treatment			Amount adhered (calculated as C) (wt. %)
	Linear load		Time (min.)	
(N/cm)	(Kg/cm)			
Example 81	588	60	20	6.04
Example 82	441	45	30	4.60
Example 83	735	75	20	8.62
Example 84	588	60	20	11.09
Example 85	294	30	30	8.61
Example 86	441	45	20	7.09
Example 87	490	50	20	4.61
Example 88	588	60	20	6.05
Comparative Example 53	588	60	20	6.05
Comparative Example 54	-	-	-	-
Comparative Example 55	588	60	20	6.03
Comparative Example 56	588	60	20	0.60
Comparative Example 57	588	60	20	6.03



Table 19

Examples and Comparative Examples	Properties of green-based fine pigment		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Example 81	0.0825	0.0100	8.3:1
Example 82	0.0580	0.0097	6.0:1
Example 83	0.0777	0.0125	6.2:1
Example 84	0.0918	0.0188	4.9:1
Example 85	0.0831	0.0102	8.1:1
Example 86	0.0585	0.0101	5.8:1
Example 87	0.0777	0.0125	6.2:1
Example 88	0.0910	0.0185	4.9:1
Comparative Example 53	0.0814	0.0096	8.5:1
Comparative Example 54	0.0813	0.0096	8.5:1
Comparative Example 55	0.0815	0.0097	8.4:1
Comparative Example 56	0.0816	0.0097	8.4:1
Comparative Example 57	0.0815	0.0097	8.4:1

Table 19 (continued)

Examples and Comparative Examples	Properties of green-based fine pigment		
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Al content <sup>*1</sup> within particles (wt. %)
Example 81	1.41	142.2	-
Example 82	1.36	189.6	2.56
Example 83	1.37	143.8	1.87
Example 84	1.41	96.0	-
Example 85	1.42	148.1	-
Example 86	1.36	180.5	2.56
Example 87	1.37	149.6	1.87
Example 88	1.41	106.2	-
Comparative Example 53	-	164.7	-
Comparative Example 54	1.41	149.2	-
Comparative Example 55	-	160.1	-
Comparative Example 56	1.41	147.6	-
Comparative Example 57	-	161.3	-

\*1: Content within core particles

Table 19 (continued)

Examples and Comparative Examples	Properties of green-based fine pigment	
	Composite oxide hydroxide	
	Coating amount of Al <sup>*1</sup> (calculated as Al) (wt. %)	Coating amount of Fe <sup>*1</sup> (calculated as Fe) (wt. %)
Example 81	-	-
Example 82	-	-
Example 83	1.13	0.64
Example 84	-	-
Example 85	-	-
Example 86	-	-
Example 87	1.13	0.64
Example 88	-	-
Comparative Example 53	-	-
Comparative Example 54	-	-
Comparative Example 55	-	-
Comparative Example 56	-	-
Comparative Example 57	-	-

\*1: Coating amount on core particles

Table 19 (continued)

Examples and Comparative Examples	Properties of green-based fine pigment			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 81	31.9	-14.2	3.8	165.0
Example 82	33.2	-11.2	5.2	155.1
Example 83	28.6	-16.8	0.6	178.0
Example 84	26.5	-16.9	-1.1	183.7
Example 85	30.1	-14.2	-1.9	187.6
Example 86	31.2	-18.2	0.4	178.7
Example 87	35.3	-10.8	6.6	148.6
Example 88	27.4	-12.0	9.1	142.8
Comparative Example 53	30.9	-9.3	4.6	153.7
Comparative Example 54	50.2	29.8	54.0	61.1
Comparative Example 55	31.2	-8.3	4.1	153.7
Comparative Example 56	31.4	10.5	30.4	70.9
Comparative Example 57	30.3	-8.0	4.4	151.2

Table 19 (continued)

Examples and Comparative Examples	Properties of green-based fine pigment			
	Tinting strength (%)	Hiding power (cm <sup>2</sup> /g)	Chemical resistances	
			Acid resistance $\Delta E^*$ value (-)	Alkali resistance $\Delta E^*$ value (-)
Example 81	133	177	1.26	1.12
Example 82	126	152	1.05	1.00
Example 83	142	176	0.98	0.91
Example 84	148	215	1.23	1.02
Example 85	146	175	1.14	1.03
Example 86	140	150	1.01	0.95
Example 87	131	158	0.95	0.87
Example 88	134	211	1.23	0.97
Comparative Example 53	110	208	2.04	1.83
Comparative Example 54	104	172	2.00	1.81
Comparative Example 55	112	203	2.04	1.81
Comparative Example 56	108	172	1.97	1.78
Comparative Example 57	111	202	1.99	1.80

Table 19 (continued)

Examples and Comparative Examples	Properties of green-based fine pigment	
	Heat resistance temperature (°C)	Desorption percentage of organic pigment (%)
Example 81	223	6.8
Example 82	259	6.1
Example 83	283	7.6
Example 84	229	8.1
Example 85	243	4.7
Example 86	267	4.6
Example 87	284	2.9
Example 88	239	3.4
Comparative Example 53	193	68.3
Comparative Example 54	197	-
Comparative Example 55	194	49.3
Comparative Example 56	197	5.7
Comparative Example 57	198	46.6

Table 20

Examples and Comparative Examples	Production of paint	Properties of paint	
	Kind of green-based fine pigment	Viscosity (cP)	Storage stability $\Delta E^*$ value (-)
Example 89	Example 81	1,690	0.93
Example 90	Example 82	1,741	0.88
Example 91	Example 83	1,997	0.77
Example 92	Example 84	1,796	0.93
Example 93	Example 85	2,124	0.61
Example 94	Example 86	1,920	0.52
Example 95	Example 87	2,560	0.47
Example 96	Example 88	2,051	0.64
Comparative Example 58	Comparative Example 53	10,240	2.24
Comparative Example 59	Comparative Example 54	2,560	1.58
Comparative Example 60	Comparative Example 55	8,960	2.03
Comparative Example 61	Comparative Example 56	2,816	1.52
Comparative Example 62	Comparative Example 57	6,656	2.00

Table 20 (continued)

Examples and Comparative Examples	Properties of coating film				
	60° gloss (%)	Hue			
		L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 89	81.6	33.3	-20.2	4.8	166.6
Example 90	85.3	35.4	-17.6	6.0	161.2
Example 91	88.2	30.1	-22.4	1.6	175.9
Example 92	81.3	27.5	-22.9	-0.8	182.0
Example 93	86.7	32.2	-21.5	-1.1	182.9
Example 94	88.1	33.8	-24.1	1.3	176.9
Example 95	91.6	36.4	-16.9	2.5	171.6
Example 96	85.4	29.6	-20.1	10.1	153.3
Comparative Example 58	65.2	32.8	-10.1	6.6	146.8
Comparative Example 59	79.8	54.3	28.6	62.3	65.3
Comparative Example 60	68.9	33.9	-11.6	5.9	153.0
Comparative Example 61	80.4	40.3	28.4	40.1	54.7
Comparative Example 62	68.5	31.1	-12.4	6.1	153.8



Table 20 (continued)

Examples and Comparative Examples	Properties of coating film	
	Chemical resistances	
	Acid resistance $\Delta G$ value (-)	Alkali resistance $\Delta G$ value (-)
Example 89	8.4	7.6
Example 90	8.0	7.1
Example 91	7.6	6.8
Example 92	9.1	8.7
Example 93	6.7	5.5
Example 94	6.4	5.2
Example 95	4.3	3.9
Example 96	6.0	5.6
Comparative Example 58	14.9	13.2
Comparative Example 59	13.1	12.6
Comparative Example 60	14.4	12.4
Comparative Example 61	12.8	12.1
Comparative Example 62	14.5	12.4

Table 20 (continued)

Examples and Comparative Examples	Properties of coating film	
	Heat resistance temperature (°C)	Transparency (linear absorption) ( $\mu\text{m}^{-1}$ )
Example 89	241	0.0296
Example 90	265	0.0182
Example 91	285	0.0262
Example 92	247	0.0360
Example 93	258	0.0251
Example 94	274	0.0177
Example 95	286	0.0194
Example 96	252	0.0312
Comparative Example 58	213	0.0892
Comparative Example 59	215	0.0532
Comparative Example 60	214	0.0823
Comparative Example 61	219	0.0666
Comparative Example 62	215	0.0834

Table 21

Examples and Comparative Examples	Production of water- based paint	Properties of paint	
	Kind of green-based fine pigment	Viscosity (cP)	Storage stability $\Delta E^*$ value (-)
Example 97	Example 81	2,867	1.00
Example 98	Example 82	3,482	0.96
Example 99	Example 83	3,200	0.87
Example 100	Example 84	3,294	1.04
Example 101	Example 85	3,123	0.71
Example 102	Example 86	2,944	0.61
Example 103	Example 87	2,816	0.55
Example 104	Example 88	2,731	0.72
Comparative Example 63	Comparative Example 53	11,385	2.38
Comparative Example 64	Comparative Example 54	3,482	1.69
Comparative Example 65	Comparative Example 55	12,800	2.26
Comparative Example 66	Comparative Example 56	3,123	1.65
Comparative Example 67	Comparative Example 57	6,400	2.21

Table 21 (continued)

Examples and Comparative Examples	Properties of coating film				
	60° gloss (%)	Hue			
		L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 97	77.8	33.5	-20.0	4.2	168.1
Example 98	80.6	35.7	-17.5	5.6	162.3
Example 99	83.2	30.6	-22.2	1.0	177.4
Example 100	76.5	27.9	-22.7	-0.9	182.3
Example 101	82.9	33.2	-21.4	-1.2	183.2
Example 102	84.0	34.2	-24.0	1.4	176.7
Example 103	87.4	36.9	-16.7	2.6	171.2
Example 104	81.1	29.7	-20.4	10.0	153.9
Comparative Example 63	60.1	33.1	-10.0	6.5	147.0
Comparative Example 64	73.2	55.3	28.3	62.9	65.8
Comparative Example 65	63.6	34.4	-11.5	6.1	152.1
Comparative Example 66	74.2	40.8	27.9	41.4	56.0
Comparative Example 67	62.3	31.7	-12.1	6.3	152.5

Table 21 (continued)

Examples and Comparative Examples	Properties of coating film	
	Chemical resistances	
	Acid resistance	Alkali resistance
	$\Delta G$ value (-)	$\Delta G$ value (-)
Example 97	8.6	8.1
Example 98	8.9	7.4
Example 99	8.0	7.2
Example 100	9.4	9.0
Example 101	7.1	5.9
Example 102	6.9	5.7
Example 103	5.0	4.3
Example 104	6.7	6.1
Comparative Example 63	15.7	14.1
Comparative Example 64	14.0	13.5
Comparative Example 65	15.5	13.4
Comparative Example 66	13.9	13.0
Comparative Example 67	15.2	13.3

Table 21 (continued)

Examples and Comparative Examples	Properties of coating film	
	Heat resistance temperature (°C)	Transparency (linear absorption) ( $\mu\text{m}^{-1}$ )
Example 97	240	0.0314
Example 98	262	0.0201
Example 99	284	0.0285
Example 100	245	0.0380
Example 101	253	0.0262
Example 102	271	0.0189
Example 103	285	0.0211
Example 104	251	0.0331
Comparative Example 63	207	0.0951
Comparative Example 64	210	0.0560
Comparative Example 65	208	0.0853
Comparative Example 66	214	0.0696
Comparative Example 67	210	0.0854

Table 22

Examples and Comparative Examples	Production of resin composition	Properties of resin composition
	Kind of green- based fine pigment	Dispersion condition (-)
Example 105	Example 81	4
Example 106	Example 82	5
Example 107	Example 83	5
Example 108	Example 84	4
Example 109	Example 85	5
Example 110	Example 86	5
Example 111	Example 87	5
Example 112	Example 88	5
Comparative Example 68	Comparative Example 53	2
Comparative Example 69	Comparative Example 54	3
Comparative Example 70	Comparative Example 55	2
Comparative Example 71	Comparative Example 56	2
Comparative Example 72	Comparative Example 57	2

Table 22 (continued)

Examples and Comparative Examples	Properties of resin composition			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 105	33.2	-17.2	6.6	159.0
Example 106	34.1	-15.6	7.1	155.5
Example 107	29.8	-18.6	3.2	170.2
Example 108	27.9	-19.5	0.7	177.9
Example 109	32.0	-19.8	-1.4	184.0
Example 110	32.3	-21.6	2.6	173.1
Example 111	36.3	-14.2	8.9	147.9
Example 112	29.7	-15.1	10.8	144.4
Comparative Example 68	32.8	-13.6	6.6	154.1
Comparative Example 69	52.3	27.0	57.3	64.8
Comparative Example 70	33.2	-12.2	6.3	152.7
Comparative Example 71	34.3	6.6	34.2	79.1
Comparative Example 72	32.1	-12.8	6.6	152.7



Table 22 (continued)

Examples and Comparative Examples	Properties of resin composition	
	Heat resistance temperature (°C)	Transparency (linear absorption) ( $\mu\text{m}^{-1}$ )
Example 105	225	0.0312
Example 106	234	0.0199
Example 107	238	0.0274
Example 108	227	0.0368
Example 109	231	0.0261
Example 110	235	0.0183
Example 111	240	0.0200
Example 112	231	0.0320
Comparative Example 68	195	0.0919
Comparative Example 69	200	0.0550
Comparative Example 70	197	0.0851
Comparative Example 71	202	0.0688
Comparative Example 72	198	0.0857

Table 23

Examples and Comparative Examples	Kind of core particles	Production of orange- based fine pigment	
		Coating step with alkoxysilane, polysiloxane or silicon compound	
		Additives	
		Kind	Amount added (part by weight)
Example 113	Core particles 9	Methyl triethoxysilane	2.0
Example 114	Core particles 10	Methyl trimethoxysilane	1.0
Example 115	Core particles 11	Phenyl triethoxysilane	1.5
Example 116	Core particles 12	Methyl hydrogen polysiloxane	1.0
Example 117	Core particles 13	Methyl triethoxysilane	2.0
Example 118	Core particles 14	Methyl triethoxysilane	1.0
Example 119	Core particles 15	Methyl triethoxysilane	1.5
Example 120	Core particles 16	Methyl triethoxysilane	2.0
Comparative Example 73	Core particles 9	-	-
Comparative Example 74	Core particles 9	Methyl triethoxysilane	1.0
Comparative Example 75	Core particles 9	Methyl triethoxysilane	0.005
Comparative Example 76	Core particles 9	Methyl triethoxysilane	1.0
Comparative Example 77	Core particles 9	$\gamma$ -aminopropyl triethoxysilane	1.0

Table 23 (continued)

Examples and Comparative Examples	Production of orange-based fine pigment			
	Coating step with alkoxysilane, polysiloxane or silicon compound			
	Edge runner treatment			Coating amount (calculated as Si) (wt. %)
	Linear load		Time (min.)	
	(N/cm)	(Kg/cm)		
Example 113	588	60	20	0.30
Example 114	588	60	20	0.19
Example 115	441	45	30	0.20
Example 116	588	60	20	0.44
Example 117	294	30	30	0.30
Example 118	588	60	20	0.15
Example 119	441	45	30	0.23
Example 120	588	60	20	0.30
Comparative Example 73	-	-	-	-
Comparative Example 74	588	60	20	0.15
Comparative Example 75	588	60	20	6 x 10 <sup>-4</sup>
Comparative Example 76	588	60	20	0.15
Comparative Example 77	588	60	20	0.12

Table 23 (continued)

Examples and Comparative Examples	Production of orange-based fine pigment	
	Adhesion step with organic red pigment	
	Organic red pigment	
	Kind	Amount adhered (part by weight)
Example 113	D	10.0
Example 114	E	15.0
Example 115	D	20.0
Example 116	E	15.0
Example 117	D	10.0
Example 118	E	5.0
Example 119	D	10.0
Example 120	E	25.0
Comparative Example 73	D	10.0
Comparative Example 74	D	100.0
Comparative Example 75	D	10.0
Comparative Example 76	D	0.5
Comparative Example 77	D	10.0

Table 23 (continued)

Examples and Comparative Examples	Production of orange-based fine pigment			
	Adhesion step with organic red pigment			
	Edge runner treatment			Amount adhered (calculated as C) (wt. %)
	Linear load		Time (min.)	
	(N/cm)	(Kg/cm)		
Example 113	588	60	20	6.93
Example 114	294	30	30	10.00
Example 115	441	45	30	12.77
Example 116	294	30	30	9.98
Example 117	588	60	20	6.91
Example 118	294	30	30	3.62
Example 119	441	45	20	6.94
Example 120	588	60	20	15.33
Comparative Example 73	588	60	20	6.92
Comparative Example 74	588	60	20	38.31
Comparative Example 75	588	60	20	6.90
Comparative Example 76	588	60	20	0.34
Comparative Example 77	588	60	20	6.91

Table 24

Examples and Comparative Examples	Properties of orange-based fine pigment		
	Average major axial diameter ( $\mu\text{m}$ )	Average minor axial diameter ( $\mu\text{m}$ )	Aspect ratio (-)
Example 113	0.0824	0.0098	8.4:1
Example 114	0.0585	0.0100	5.9:1
Example 115	0.0783	0.0127	6.2:1
Example 116	0.0913	0.0186	4.9:1
Example 117	0.0829	0.0102	8.1:1
Example 118	0.0579	0.0097	6.0:1
Example 119	0.0777	0.0125	6.2:1
Example 120	0.0919	0.0193	4.8:1
Comparative Example 73	0.0815	0.0096	8.5:1
Comparative Example 74	0.0849	0.0107	7.9:1
Comparative Example 75	0.0816	0.0097	8.4:1
Comparative Example 76	0.0814	0.0096	8.5:1
Comparative Example 77	0.0817	0.0097	8.4:1

Table 24 (continued)

Examples and Comparative Examples	Properties of orange-based fine pigment		
	Geometrical standard deviation value (-)	BET specific surface area value (m <sup>2</sup> /g)	Al content* <sup>1</sup> within particles (wt. %)
Example 113	1.41	151.2	-
Example 114	1.35	190.6	2.56
Example 115	1.36	150.6	1.87
Example 116	1.41	100.6	-
Example 117	1.41	152.6	-
Example 118	1.35	184.3	2.56
Example 119	1.37	152.1	1.87
Example 120	1.42	111.1	-
Comparative Example 73	-	135.8	-
Comparative Example 74	-	146.8	-
Comparative Example 75	-	140.4	-
Comparative Example 76	1.41	141.2	-
Comparative Example 77	-	146.6	-

\*1: Content within core particles

Table 24 (continued)

Examples and Comparative Examples	Properties of orange-based fine pigment	
	Composite oxide hydroxide	
	Coating amount of Al <sup>*1</sup> (calculated as Al) (wt. %)	Coating amount of Fe <sup>*1</sup> (calculated as Fe) (wt. %)
Example 113	-	-
Example 114	-	-
Example 115	1.13	0.64
Example 116	-	-
Example 117	-	-
Example 118	-	-
Example 119	1.13	0.64
Example 120	-	-
Comparative Example 73	-	-
Comparative Example 74	-	-
Comparative Example 75	-	-
Comparative Example 76	-	-
Comparative Example 77	-	-

\*1: Coating amount on core particles



Table 24 (continued)

Examples and Comparative Examples	Properties of orange-based fine pigment			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 113	34.6	49.1	38.0	37.7
Example 114	35.1	49.4	36.8	36.7
Example 115	34.4	49.3	33.7	34.4
Example 116	32.1	50.1	35.5	35.3
Example 117	35.6	49.2	37.6	37.4
Example 118	43.2	40.6	42.4	46.2
Example 119	38.9	48.4	38.9	38.8
Example 120	31.0	50.9	31.1	31.4
Comparative Example 73	35.1	46.7	40.6	41.0
Comparative Example 74	28.3	51.2	23.4	24.6
Comparative Example 75	34.9	47.2	39.9	40.2
Comparative Example 76	46.2	32.9	51.4	57.4
Comparative Example 77	34.8	47.3	39.7	40.0

Table 24 (continued)

Examples and Comparative Examples	Properties of orange-based fine pigment			
	Tinting strength (%)	Hiding power (cm <sup>2</sup> /g)	Chemical resistances	
			Acid resistance $\Delta E^*$ value (-)	Alkali resistance $\Delta E^*$ value (-)
Example 113	128	180	1.27	1.18
Example 114	132	152	1.08	1.00
Example 115	136	172	0.99	0.96
Example 116	126	223	1.29	1.21
Example 117	131	176	1.16	1.09
Example 118	130	145	1.06	0.98
Example 119	134	161	0.94	0.91
Example 120	133	224	1.21	1.13
Comparative Example 73	100	197	2.04	1.81
Comparative Example 74	116	266	1.74	1.66
Comparative Example 75	102	190	2.00	1.76
Comparative Example 76	106	174	1.82	1.71
Comparative Example 77	104	189	1.99	1.74

Table 24 (continued)

Examples and Comparative Examples	Properties of orange-based fine pigment	
	Heat resistance temperature (°C)	Desorption percentage of organic pigment (%)
Example 113	224	7.1
Example 114	253	8.3
Example 115	276	9.2
Example 116	226	8.7
Example 117	238	3.9
Example 118	267	2.2
Example 119	281	2.6
Example 120	230	4.8
Comparative Example 73	194	69.4
Comparative Example 74	231	60.1
Comparative Example 75	197	57.2
Comparative Example 76	200	6.8
Comparative Example 77	199	56.6

Table 25

Examples and Comparative Examples	Production of paint	Properties of paint	
	Kind of orange-based fine pigment	Viscosity (cP)	Storage stability $\Delta E^*$ value (-)
Example 121	Example 113	3,580	0.96
Example 122	Example 114	3,180	0.92
Example 123	Example 115	2,863	0.81
Example 124	Example 116	3,265	0.99
Example 125	Example 117	3,384	0.93
Example 126	Example 118	3,062	0.90
Example 127	Example 119	3,056	0.77
Example 128	Example 120	2,786	0.97
Comparative Example 78	Comparative Example 73	12,560	2.34
Comparative Example 79	Comparative Example 74	3,183	1.60
Comparative Example 80	Comparative Example 75	2,965	2.30
Comparative Example 81	Comparative Example 76	2,872	1.65
Comparative Example 82	Comparative Example 77	3,682	2.28

Table 25 (continued)

Examples and Comparative Examples	Properties of coating film				
	60° gloss (%)	Hue			
		L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 121	81.7	35.8	48.3	38.0	38.2
Example 122	86.1	36.4	48.5	36.6	37.0
Example 123	88.9	36.3	48.6	33.8	34.8
Example 124	81.2	33.6	49.3	35.7	35.9
Example 125	87.0	36.8	48.6	37.6	37.7
Example 126	88.8	44.1	39.8	42.3	46.7
Example 127	92.3	40.3	47.7	39.1	39.3
Example 128	85.7	32.3	50.1	30.9	31.7
Comparative Example 78	64.6	36.6	45.3	40.2	41.6
Comparative Example 79	58.5	29.9	50.2	23.5	25.1
Comparative Example 80	68.0	36.3	46.3	39.4	40.4
Comparative Example 81	80.3	47.6	31.8	51.1	58.1
Comparative Example 82	68.9	36.1	46.3	39.2	40.3

Table 25 (continued)

Examples and Comparative Examples	Properties of coating film	
	Chemical resistances	
	Acid resistance	Alkali resistance
	$\Delta G$ value (-)	$\Delta G$ value (-)
Example 121	8.9	8.1
Example 122	8.4	7.6
Example 123	7.7	6.8
Example 124	9.2	8.4
Example 125	8.5	7.8
Example 126	8.2	7.1
Example 127	5.1	4.6
Example 128	8.7	7.9
Comparative Example 78	15.1	14.7
Comparative Example 79	12.6	12.1
Comparative Example 80	14.7	14.2
Comparative Example 81	13.4	13.6
Comparative Example 82	14.7	14.0

Table 25 (continued)

Examples and Comparative Examples	Properties of coating film	
	Heat resistance temperature (°C)	Transparency (linear absorption) ( $\mu\text{m}^{-1}$ )
Example 121	243	0.0300
Example 122	261	0.0186
Example 123	281	0.0260
Example 124	246	0.0362
Example 125	254	0.0261
Example 126	273	0.0170
Example 127	283	0.0199
Example 128	248	0.0332
Comparative Example 78	208	0.0872
Comparative Example 79	246	0.1032
Comparative Example 80	215	0.0828
Comparative Example 81	216	0.0296
Comparative Example 82	217	0.0816

Table 26

Examples and Comparative Examples	Production of water- based paint	Properties of paint	
	Kind of orange-based fine pigment	Viscosity (cP)	Storage stability $\Delta E^*$ value (-)
Example 129	Example 113	3,670	1.03
Example 130	Example 114	3,281	0.98
Example 131	Example 115	3,659	0.88
Example 132	Example 116	3,263	1.05
Example 133	Example 117	3,486	1.00
Example 134	Example 118	3,365	0.96
Example 135	Example 119	4,163	0.81
Example 136	Example 120	3,887	1.04
Comparative Example 83	Comparative Example 73	11,197	2.45
Comparative Example 84	Comparative Example 74	3,663	1.69
Comparative Example 85	Comparative Example 75	2,816	2.41
Comparative Example 86	Comparative Example 76	3,162	1.72
Comparative Example 87	Comparative Example 77	3,386	2.38



Table 26 (continued)

Examples and Comparative Examples	Properties of coating film				
	60° gloss (%)	Hue			
		L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 129	77.5	35.9	48.8	38.3	38.1
Example 130	81.4	36.6	48.2	36.6	37.2
Example 131	84.2	36.2	48.5	33.8	34.9
Example 132	76.9	33.5	49.6	35.8	35.8
Example 133	81.8	36.6	48.9	37.9	37.8
Example 134	83.9	43.9	39.8	42.0	46.5
Example 135	87.5	40.6	48.0	39.3	39.3
Example 136	81.3	32.6	50.1	31.0	31.7
Comparative Example 83	60.1	36.8	45.8	40.4	41.4
Comparative Example 84	53.4	29.8	50.3	23.7	25.2
Comparative Example 85	63.0	36.3	46.6	39.6	40.4
Comparative Example 86	75.8	47.1	32.2	51.6	58.0
Comparative Example 87	64.0	36.3	46.6	39.3	40.1

Table 26 (continued)

Examples and Comparative Examples	Properties of coating film	
	Chemical resistances	
	Acid resistance	Alkali resistance
	$\Delta G$ value (-)	$\Delta G$ value (-)
Example 129	9.2	8.3
Example 130	8.6	7.5
Example 131	8.0	7.0
Example 132	9.6	8.7
Example 133	8.7	8.1
Example 134	8.3	7.3
Example 135	5.4	5.0
Example 136	8.7	8.2
Comparative Example 83	15.6	15.0
Comparative Example 84	12.9	12.4
Comparative Example 85	15.1	14.6
Comparative Example 86	13.5	13.9
Comparative Example 87	14.9	14.4

Table 26 (continued)

Examples and Comparative Examples	Properties of coating film	
	Heat resistance temperature (°C)	Transparency (linear absorption) ( $\mu\text{m}^{-1}$ )
Example 129	240	0.0319
Example 130	259	0.0204
Example 131	278	0.0280
Example 132	243	0.0377
Example 133	250	0.0282
Example 134	271	0.0188
Example 135	279	0.0216
Example 136	244	0.0353
Comparative Example 83	204	0.0893
Comparative Example 84	240	0.1051
Comparative Example 85	211	0.0849
Comparative Example 86	214	0.0314
Comparative Example 87	212	0.0833

Table 27

Examples and Comparative Examples	Production of resin composition	Properties of resin composition
	Kind of orange- based fine pigment	Dispersion condition (-)
Example 137	Example 113	4
Example 138	Example 114	5
Example 139	Example 115	5
Example 140	Example 116	5
Example 141	Example 117	5
Example 142	Example 118	5
Example 143	Example 119	5
Example 144	Example 120	5
Comparative Example 88	Comparative Example 73	2
Comparative Example 89	Comparative Example 74	3
Comparative Example 90	Comparative Example 75	2
Comparative Example 91	Comparative Example 76	3
Comparative Example 92	Comparative Example 77	2

Table 27 (continued)

Examples and Comparative Examples	Properties of resin composition			
	Hue			
	L* value (-)	a* value (-)	b* value (-)	h value (°)
Example 137	35.8	49.5	38.7	38.0
Example 138	36.1	48.9	37.5	37.5
Example 139	36.6	49.6	35.0	35.2
Example 140	33.8	50.6	36.8	36.0
Example 141	36.9	49.9	39.2	38.2
Example 142	44.0	40.7	43.8	47.1
Example 143	40.5	49.1	40.3	39.4
Example 144	32.9	51.6	32.2	32.0
Comparative Example 88	36.9	46.5	41.6	41.8
Comparative Example 89	29.9	51.5	24.6	25.5
Comparative Example 90	36.1	47.9	41.0	40.6
Comparative Example 91	47.2	32.6	52.6	58.2
Comparative Example 92	36.5	48.0	40.2	39.9

Table 27 (continued)

Examples and Comparative Examples	Properties of resin composition	
	Heat resistance temperature (°C)	Transparency (linear absorption) ( $\mu\text{m}^{-1}$ )
Example 137	223	0.0318
Example 138	231	0.0203
Example 139	236	0.0284
Example 140	228	0.0356
Example 141	235	0.0273
Example 142	237	0.0180
Example 143	239	0.0212
Example 144	225	0.0352
Comparative Example 88	195	0.0889
Comparative Example 89	201	0.1045
Comparative Example 90	197	0.0842
Comparative Example 91	199	0.0310
Comparative Example 92	198	0.0828

# Claims

1. Iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , each comprising:

- (a) an iron oxide hydroxide core;
- (b) a coating formed on a surface of said core and comprising

(1) one or more organosilane compounds obtainable from alkoxysilane compounds, and/or

(2) one or more polysiloxanes or modified polysiloxanes; and

(c) an organic pigment coat formed on said coating (b) in an amount of from 1 to 30 parts by weight based on 100 parts by weight of the core (a).

2. Particles according to claim 1, wherein each core comprises an iron oxide hydroxide particle having a coat formed on at least a part of a surface thereof, the coat comprising at least one of hydroxides of aluminum, oxides of aluminum, hydroxides of silicon and oxides of silicon in an amount of 0.01 to 20% by weight, calculated as Al or SiO<sub>2</sub>, based on the total weight of the iron oxide hydroxide particles coated.

3. Particles according to claim 1 or 2, wherein said modified polysiloxanes are:

(A) polysiloxanes modified with at least one of polyethers, polyesters and epoxy compounds, and/or  
(B) polysiloxanes whose molecular terminal is modified with at least one of carboxylic acid groups, alcohol groups and a hydroxyl group.

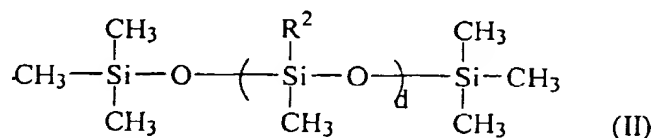
4. Particles according to claim 1, 2 or 3, wherein said alkoxysilane compound is represented by the general formula (I):



wherein R<sup>1</sup> is C<sub>6</sub>H<sub>5</sub>-, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>- or n-C<sub>b</sub>H<sub>2b+1</sub>- (wherein b is an integer of 1 to 18); X is CH<sub>3</sub>O- or C<sub>2</sub>H<sub>5</sub>O-; and a is 0 or an integer of 1 to 3.

5. Particles according to claim 4, wherein said alkoxysilane compound is methyltriethoxysilane, dimethyldiethoxysilane, phenyltriethoxysilane, diphenyldiethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane, isobutyltrimethoxysilane or decyltrimethoxysilane.

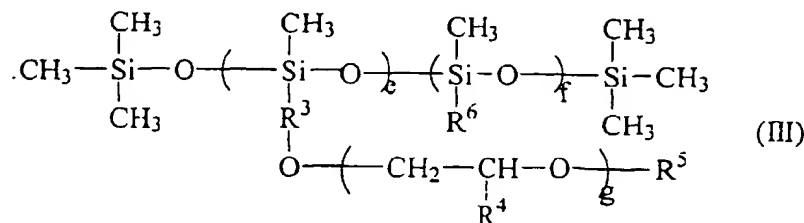
6. Particles according to any preceding claim, wherein said polysiloxanes are represented by the general formula (II):



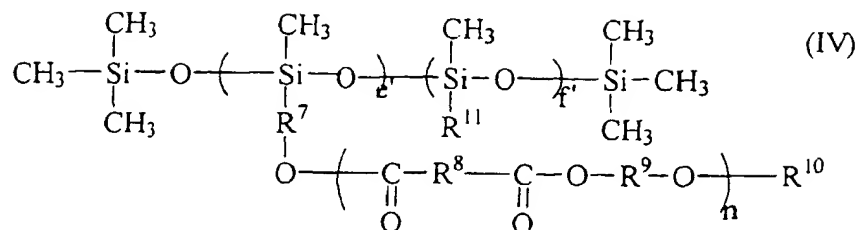
wherein R<sup>2</sup> is H- or CH<sub>3</sub>-, and d is an integer of 15 to 450.

7. Particles according to claim 6, wherein said polysiloxanes are compounds having methyl hydrogen siloxane units.

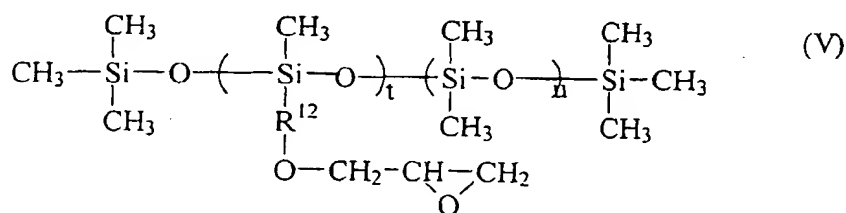
8. Particles according to claim 3, wherein said polysiloxanes are represented by the general formula (III), (IV) or (V):



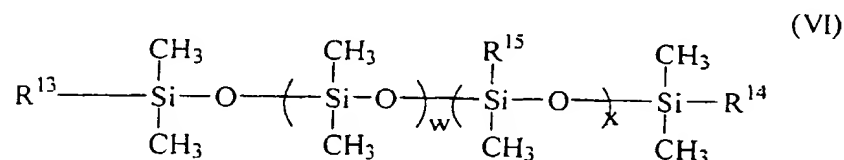
wherein R<sup>3</sup> is -(CH<sub>2</sub>)<sub>h</sub>-; R<sup>4</sup> is -(CH<sub>2</sub>)<sub>i</sub>-CH<sub>3</sub>; R<sup>5</sup> is -OH, -COOH, -CH=CH<sub>2</sub>, -C(CH<sub>3</sub>)=CH<sub>2</sub> or -(CH<sub>2</sub>)<sub>j</sub>-CH<sub>3</sub>; R<sup>6</sup> is -(CH<sub>2</sub>)<sub>k</sub>-CH<sub>3</sub>; each of g and h is an integer of 1 to 15; each of i, j and k is 0 or an integer of 1 to 15; e is an integer of 1 to 50; and f is an integer of 1 to 300;



wherein  $\text{R}^7$ ,  $\text{R}^8$  and  $\text{R}^9$  are  $-(\text{CH}_2)_q-$  and may be the same or different;  $\text{R}^{10}$  is  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{C}(\text{CH}_3)=\text{CH}_2$  or  $-(\text{CH}_2)_r-\text{CH}_3$ ;  $\text{R}^{11}$  is  $-(\text{CH}_2)_s-\text{CH}_3$ ; each of  $n$  and  $q$  is an integer of 1 to 15; each of  $r$  and  $s$  is 0 or an integer of 1 to 15;  $e$  is an integer of 1 to 50; and  $f$  is an integer of 1 to 300;



wherein  $\text{R}^{12}$  is  $-(\text{CH}_2)_v-$ ;  $v$  is an integer of 1 to 15;  $t$  is an integer of 1 to 50; and  $u$  is an integer of 1 to 300;



wherein each  $\text{R}^{13}$  and  $\text{R}^{14}$  is  $-\text{OH}$ ,  $\text{R}^{16}\text{OH}$  or  $\text{R}^{17}\text{COOH}$  and may be the same or different;  $\text{R}^{15}$  is  $-\text{CH}_3$  or  $-\text{C}_6\text{H}_5$ ; each of  $\text{R}^{16}$  and  $\text{R}^{17}$  is  $-(\text{CH}_2)_y-$ ;  $y$  is an integer of 1 to 15;  $w$  is an integer of 1 to 200; and  $x$  is 0 or an integer of 1 to 100.

9. Particles according to any preceding claim, wherein the amount of the coating (b) is 0.02 to 5.0% by weight, calculated as Si, based on the total weight of the coating (b) and core (a).
10. Particles according to any preceding claim, wherein the pigment (c) is an organic blue-based pigment or an organic red-based pigment.
11. Particles according to any preceding claim, having an aspect ratio (average major axis diameter/average minor axis diameter) of 2.0:1 to 20.0:1.
12. Particles according to any preceding claim, having a BET specific surface area value of 6 to 300  $\text{m}^2/\text{g}$ .
13. Particles according to any preceding claim, having a geometrical standard deviation of major axis diameter of 1.01 to 2.0.
14. Particles according to any preceding claim, having an average particle diameter of less than 0.1  $\mu\text{m}$ ; and, where the pigment (c) is a blue-based pigment, said amount in which it is formed is at least 5 parts by weight.
15. Particles according to any of claims 1-13, having an average particle diameter of at least 0.1  $\mu\text{m}$ ; and, where the pigment (c) is a blue-based pigment, said amount in which it is formed is at least 5 parts by weight.



16. Particles according to any preceding claim, wherein the pigment (c) is an organic blue-based pigment comprising a phthalocyanine-based pigment and/or an alkali blue pigment, or is an organic red-based pigment comprising quinacridone-based pigment, azo-based pigment, condensed axo-based pigment and/or perylene-based pigment.

17. A pigment comprising particles according to any preceding claim.

18. A green-based pigment comprising particles according to claim 14 or 15 wherein the pigment (c) is a blue-based pigment.

19. An orange-based pigment comprising particles according to claim 14 to 15 wherein the pigment (c) is a red-based pigment.

20. A paint comprising:  
a pigment according to claim 17, 18 or 19; and a paint base material.

21. A paint according to claim 20, wherein the amount of said pigment is 0.5 to 100 parts by weight based on 100 parts by weight of said paint base material.

22. A rubber or resin composition comprising:  
a pigment according to claim 17, 18 or 19; and  
a base material for a rubber or resin composition.

23. A rubber or resin composition according to claim 22, wherein the amount of said pigment is 0.01 to 200 parts by weight based on 100 parts by weight of said base material for a rubber or resin composition.

24. A process for producing particles according to any of claims 1-16, which process comprises:

(a) mixing as core particles iron oxide hydroxide particles having an average particle diameter of 0.005 to 1.0µm together with

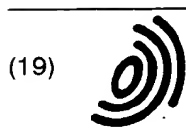
- (1) one or more alkoxysilane compounds, and/or
- (2) one or more polysiloxanes or modified polysiloxanes,

by using an apparatus capable of applying a shear force to the core particles, thereby coating a surface of the core particles with the compounds (1) and/or (2); and

(b) mixing the resulting coated particles with an organic pigment in an amount of 1 to 30 parts by weight based on 100 parts by weight of the core particles by using an apparatus capable of applying a shear force to the core particles, thereby forming an organic pigment coat on the surface of the coating layer resulting from step (a).

25. A process according to claim 24 for producing black iron oxide hydroxide composite particles wherein the core particles are coated with at least one of hydroxides of aluminum, oxides or aluminum, hydroxides of silicon and oxides of silicon.

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(54) **Iron oxide hydroxide composite particles, pigment, paint and resin composition.**

(57) Iron oxide hydroxide composite particles having an average particle diameter of 0.005 to 1.0  $\mu\text{m}$ , comprises:

iron oxide hydroxide particles as core particles,  
a coating formed on surface of said iron oxide hydroxide particles, comprising at least one organosilicon compound selected from the group consisting of:

- (1) organosilane compounds obtainable from alkoxysilane compounds, and
- (2) polysiloxanes or modified polysiloxanes, and

an organic pigment coat formed on said coating layer

comprising said organosilicon compound, in an amount of from 1 to 30 parts by weight based on 100 parts by weight of said iron oxide hydroxide particles.

The iron oxide hydroxide composite particles of the present invention contain no harmful elements and exhibit not only excellent chemical resistances such as acid resistance and alkali resistance, but also excellent heat resistance.

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## EUROPEAN SEARCH REPORT

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EP 00 31 0958

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 3 869 298 A (SUZUKI MORIO ET AL) 4 March 1975 (1975-03-04) * claims 1-6 *	1-25	C09C1/24 C09D1/00 C08K3/00 C09K3/00
A	EP 0 913 431 A (TODA KOGYO CORP) 6 May 1999 (1999-05-06) * claims 1-20; example 1 *	1-25	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C09C C09D C09K
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>16 October 2003</b>	Examiner <b>Wengeler, H</b>
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Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 3869298	A	04-03-1975	JP	884194 C	30-09-1977
			JP	48055217 A	03-08-1973
			JP	51007176 B	05-03-1976
			DE	2255464 A1	17-05-1973
			GB	1407057 A	24-09-1975
-----					
EP 0913431	A	06-05-1999	DE	69806560 D1	22-08-2002
			DE	69806560 T2	28-11-2002
			EP	0913431 A2	06-05-1999
			JP	11323174 A	26-11-1999
			US	6420030 B1	16-07-2002
-----					

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